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Powdered Activated Carbon Adsorption Isotherms for Selected Tannery Effluents

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POWDERED ACTIVATED CARBON ADSORPTION ISOTHERMS FOR SELECTED TANNERY EFFLUENTS

by

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Two raw untreated tanning effluents were initially tested for the removal of COD, BOD, TOC, total and specific phenols, oil and grease, and total chromium, using the following six individual powdered activated carbons (PAC): ICI-HDC, ICI-HDH, Nuchar SA-15, Amoco PX-21, Norit FQA, and Westates WO-841. The first three carbons were subsequently tested for the above parameters on eight additional tanning effluents, representing a total of six tanning subcategories. The carbon dose range investigated was 0.3 to 10 g/l. Final comparisons between the carbons were performed in terms of their removal efficiencies and ultimate capacities, using Freundlich adsorption isotherms.

Comparison of the wastewater characteristics of tanneries within the same subcategory indicated no similarities in the concentration of wastewater constituents. Analysis of the adsorption data indicated that the PAC's have limited ability to bind COD, BOD, TOC, THA, chromium, and oil and grease in tannery effluents. Furthermore, there was no apparent correlation between final effluent characteristics and the nature of the tanning operations.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes work undertaken to develop powdered activated carbon (PAC) adsorption isotherms on selected leather tanning effluents. The results can be used as a source of technical data to compare the relative merits of utilizing PAC to remove selected constituents from tannery waste streams. For further information, contact the Food and Wood Products Branch, IERL, Cincinnati, Ohio.

David G. Stephan
Director
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Cincinnati

ABSTRACT

This project was initiated to gain a better understanding of powdered activated carbon (PAC) addition to secondary treatment of tannery effluents. The purpose of this research was to obtain sufficient bench-scale data to select PAC's for full-scale testing. Adsorption isotherms were developed for COD, BOD, TOC, total and specific phenols, oil and grease, and total chromium.

Initially, two raw untreated tanning effluents (representing two different tanning subcategories, as classified by EPA) were tested using the following six individual PAC's: ICI-HDC, ICI-HDH, Nuchar SA-15, Amoco PX-21, Norit FQA, and Westates WO-841. The results revealed low removal efficiencies for Westates WO-841 and Norit FQA; these carbons were thus excluded from further testing. Amoco PX-21, though very efficient in the treatment of tannery effluents, was also excluded from further testing, as it is not commercially available.

The three remaining carbons (i.e., ICI-HDC, ICI-HDH, and Nuchar SA-15) were subsequently tested for the above parameters on eight additional tanning effluents (representing a total of six tanning subcategories). The carbon dose range investigated was 0.3 to 10 g/l.

Final comparisons between the individual carbons were performed in terms of their removal efficiencies (at a dose of 0.3 g/l) and ultimate capacities, using Freundlich adsorption isotherms. Freundlich adsorption isotherms were developed as the lines of best fit through each data set by performing a least squares linear regression using logarithms of the data points. Percent adsorption calculations at different doses were determined from the lines of best fit by using a computer program based on the method of flexible polyhedron search.

COD, BOD, and THA removal efficiencies of any of the three carbons at a dose of 0.3 g/l were found to be up to 30 percent for Tanneries 1, 2, 4, 5, 6, 7, 8, and 9, while PAC treatment of effluents from Tanneries 0 and 3 resulted in more than 30 percent removal of COD and THA.

In terms of ultimate surface capacities for COD, BOD, and THA within Tanneries 0, 2, 3, 7, and 9, all three carbons exhibited differences equal to or less than one order of magnitude; for Tanneries 1, 4, 5, 6, and 8, differences between ultimate capacities were found to be greater than one order of magnitude.

Four specific chlorophenols were considered in these investigations: pentachlorophenol, 2,4,5-trichlorophenol, tetrachlorophenol, and 2,4-dichlorophenol. Their presence and removal by PAC sorption were examined for Tannery 5 and 7 effluents only. All three carbons essentially removed most of the identified specific phenols from Tannery 5 effluent, but had no observable effect on the effluent from Tannery 7.

Accountable decreases in TOC concentrations were observed only at high carbon doses, indicating low efficiencies of all three carbons for the removal of TOC from all effluents tested.

Interpretation of the chromium results was not possible due to the lack of available information on both the chemical speciation of chromium and the chemical characterization of the respective effluents.

All of the PAC's tested were essentially ineffective with respect to oil and grease removals.

Comparison of the wastewater characteristics of the four pairs of tanneries within the same subcategory indicated no similarities in the concentration of wastewater constituents. Analysis of the adsorption data indicated that the PAC's have limited ability to bind COD, BOD, TOC, THA, chromium, and oil and grease in tannery effluents. Furthermore, there was no apparent correlation between final effluent characteristics and the nature of the tanning operations.

Since data on the removal of specific phenols were insufficient to draw any general conclusions, the relationship between PAC dosage and specific phenols merits further investigation. However, any future related PAC research efforts should be conducted on an effluent-by-effluent basis.

This report was submitted in fulfillment of Grant Nos. 68-03-2578, WD 7, and 68-03-3028, WA 11, by SCS Engineers under sponsorship of the U.S. Environmental Protection Agency. This report covers the period from April 9, 1979, to December 8, 1981, and work was completed in October 1980.

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It is also appropriate to acknowledge the direction and assistance of Messrs. Brian Westfall and Donald L. Wilson of the U.S. Environmental Protection Agency whose capable guidance was essential to the project.

SECTION 1

INTRODUCTION

BACKGROUND

Tanneries as a whole are considered pollution-intensive industrial complexes which generate large volumes of highly concentrated wastewater (1). In implementing Best Available Technology Economically Achievable (BATEA) and Best Conventional Pollutant Control Technology (BCT) limitations, the U.S. Environmental Protection Agency (EPA) has recommended the use of powdered activated carbon (PAC) to enhance secondary biological treatment. Several studies have shown that by adding PAC to aeration basins, the carbon and microorganisms set up a synergism that can remove pollutants more effectively than conventional secondary biological treatment systems.

The addition of PAC to activated sludge systems has reportedly had the following beneficial effects:

- Reduction of aerator and effluent foam.
- Improved solids settling.
- Increase in effective digestor capacity.
- Adsorption of color.
- Increased removal of COD, BOD, TOC, and selected organics.

Under a separate EPA grant (Grant No. S804504), the A. C. Lawrence Company was to evaluate the effectiveness of adding PAC to its activated sludge system in Winchester, New Hampshire. This project was funded by the Effluent Guidelines Division (EGD) to gain a better understanding of PAC usage for full-scale testing. The development of adsorption isotherms was initiated under this grant to obtain a sufficient data base from which to select PAC's for the full-scale testing program. While the results of these first isotherm tests are covered in a separate report, carbon selection, analytical parameters, and much of the testing protocol were developed during the early stages of the grant. The thrust of the project covered by this report, therefore, was a continuation and expansion of the work started under the A. C.

Lawrence grant. In addition, the results of this work were subsequently used to select PAC's for the full-scale tests in Winchester.

The specific objectives of this project were as follows:

- Develop adsorption isotherms for six individual PAC's on two raw, untreated tanning effluents. Parameters to be investigated include COD, BOD_5, TOC, total and specific phenols, oil and grease, and total chromium.
- Select the three best PAC's from the above, and develop adsorption isotherms on eight additional tanning effluents for the parameters shown.
- Based on the adsorption isotherm results, recommend specific PAC's for full-scale testing by the A. C. Lawrence Company.

REPORT ORGANIZATION

In the presentation that follows, the conclusions of this study and the resulting recommendations are given in Sections 2 and 3, respectively. Section 4 outlines sampling, analytical, and experimental procedures employed during this study, with more details contained in Appendix B. Section 4 also contains a brief description of adsorption isotherm calculations. The results of this research are presented and interpreted in the form of adsorption isotherms in Section 5. More details on experimental data are given in Appendix A. Costs of PAC addition to biological treatment of tannery effluents, estimated from the results discussed in Section 5, are given in Section 6. Finally, for a better understanding of the processes which generate the wastes ultimately sampled, Appendix C provides a brief description of the subcategories within the tanning industry.

SECTION 2

CONCLUSIONS

This section presents the conclusions of this study, involving the removal of different constituents from effluents generated by 10 tanneries, using the following six activated carbons: ICI-HDC, ICI-HDH, Nuchar SA-15, Norit FQA, Westates WO-841, and Amoco PX-21. For each tannery effluent, all of the carbons were examined in terms of their respective ultimate capacities and percent removals of each constituent at different carbon doses. In the delineation that follows, the term "ultimate capacity" implies the theoretical weight of the constituent adsorbed per unit weight of carbon when the carbon is in equilibrium with the surrounding solution. Ultimate capacities were determined by the lines of best fit through each data set by performing a least squares linear regression using logarithms of the data points. Percent adsorption at different carbon doses was then calculated from the lines of best fit by using a computer program based on the method of flexible polyhedron search.

The conclusions are categorized under the following headings:

- Powdered Activated Carbon (PAC).
- Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and Total Hydroxylated Aromatics (THA).
- Specific Phenols (pentachlorophenol, 2,4,5-trichlorophenol, tetrachlorophenol, and 2,4-dichlorophenol).
- Total Organic Carbon (TOC).
- Chromium.
- Oil and Grease.
- Cost Estimates.

PAC

Initial tests were performed with six activated carbons on Tanneries 0 and 4. The results revealed that Westates WO-841 and Norit FQA yield low removal efficiencies. These carbons were thus excluded from further testing. Amoco PX-21, although very efficient in the treatment of tannery effluents, was also excluded from further testing, because it is not commercially available. Consequently, effluents from the other tanneries were treated with only three carbons: ICI-HDC, ICI-HDH, and Nuchar SA-15.

COD, BOD, AND THA

The removal efficiencies of any of the three carbons at a dose of 0.3 g/l are illustrated in Figures 1a, b, c, d, and e, and 2a, b, c, d, and e. Removal of COD, BOD, and THA at the above carbon dose (regardless of carbon type) was found to be up to 30 percent from Tanneries 1, 2, 4, 5, 6, 7, 8, and 9, while PAC treatment of effluents from Tanneries 0 and 3 resulted in more than 30 percent removal of COD and THA.

Numerical values for COD removal efficiencies at a 0.3 g/l carbon dose were found to be in the following ranges: ICI-HDH, 3 to 17 percent; ICI-HDC, 4 to 18 percent; Nuchar SA-15, 7 to 36 percent. For 7 out of 10 cases (Tanneries 1, 2, 3, 5, 6, 7, 8, and 9), all three carbons yielded results that differed only up to 10 percent; for Tanneries 0, 4, and 8, however, Nuchar SA-15 accomplished removals that were 14 to 26 percent higher than those with ICI carbons.

In the case of BOD, all three carbons exhibited similar removal percentages (i.e., within a 10 percent range of difference) in 5 out of 10 cases (Tanneries 1, 3, 4, 7, and 9). For Tanneries 2, 5, 6, and 8, Nuchar SA-15 yielded 10 to 24 percent higher BOD removals than those accomplished using ICI carbons, while for Tannery 0, ICI carbons yielded 13 to 18 percent better removals than those with Nuchar SA-15.

With regard to THA removals, all three carbons yielded comparable results (equal to or less than 5 percent difference) in 8 out of 10 cases (Tanneries 1, 2, 4, 5, 6, 7, 8, and 9). For Tannery 0, Nuchar SA-15 was apparently more effective, removing 11 to 19 percent more THA compounds than ICI carbons. In the case of Tannery 3, however, ICI carbons yielded 28 to 33 percent better THA removals than Nuchar SA-15.

In terms of ultimate surface capacities (as illustrated in Figures 3a, b, c, d, and e, and 4a, b, c, d, and e), the following general observations can be made.

The highest ultimate capacity for COD removal in Tannery 0 effluent was exhibited by Nuchar SA-15 (0.8 g COD/g carbon), followed by ICI-HDC (0.4 g COD/g carbon), and ICI-HDH (0.15 g COD/g carbon). The ultimate capacities of these carbons for BOD removal were found to be in the following descending order: ICI-HDC, ICI-HDH, and Nuchar SA-15, ranging from approximately 0.3 to 0.4 g BOD/g carbon. Those for THA removal were higher for Nuchar SA-15 and ICI-HDC (0.08 g THA/g carbon) than for ICI-HDH (0.04 g THA/g carbon).

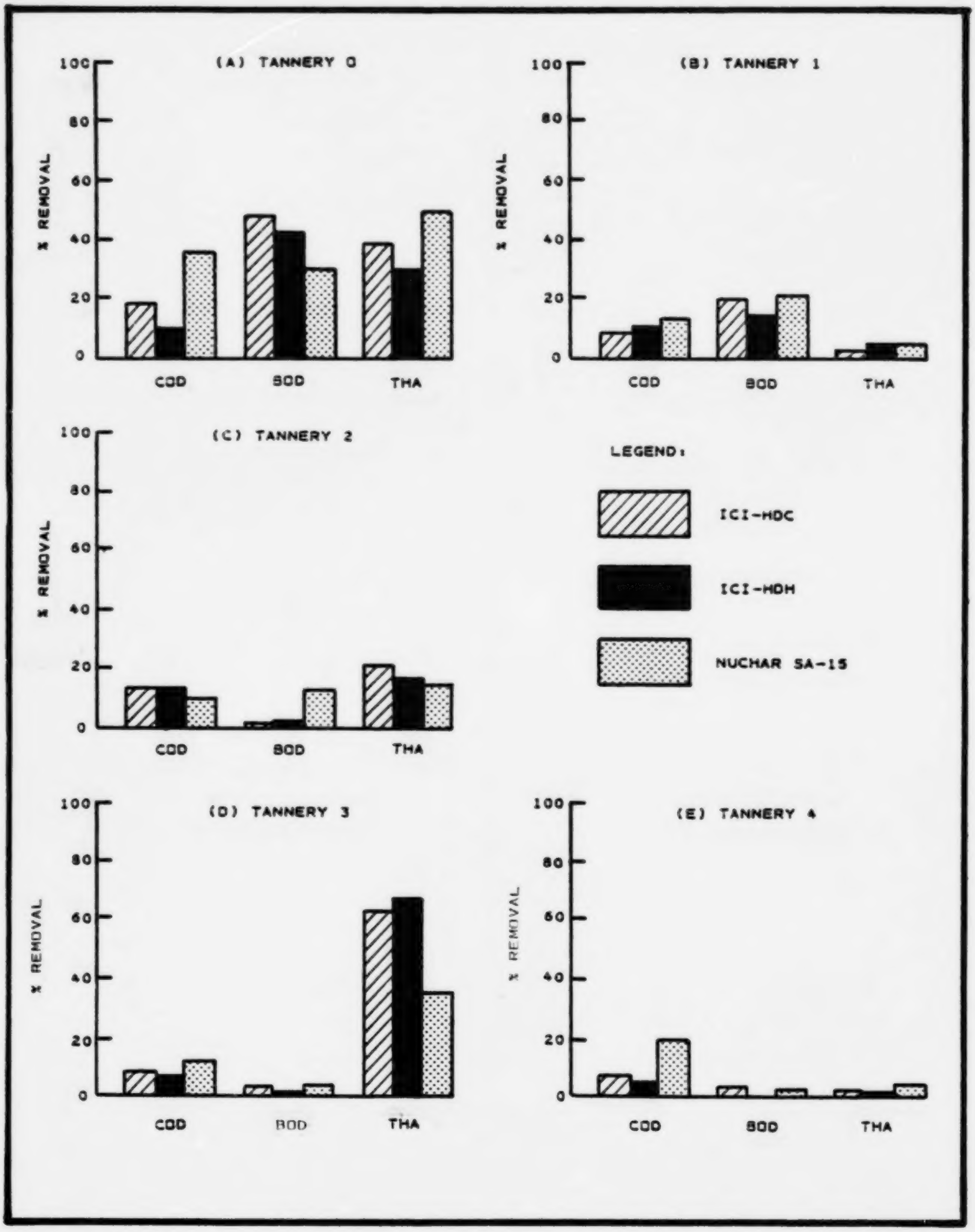

Figure 1. Percent removal of COD, BOD, and THA from Tanneries 0 through 4 effluents using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons at 0.3 g/l dose.

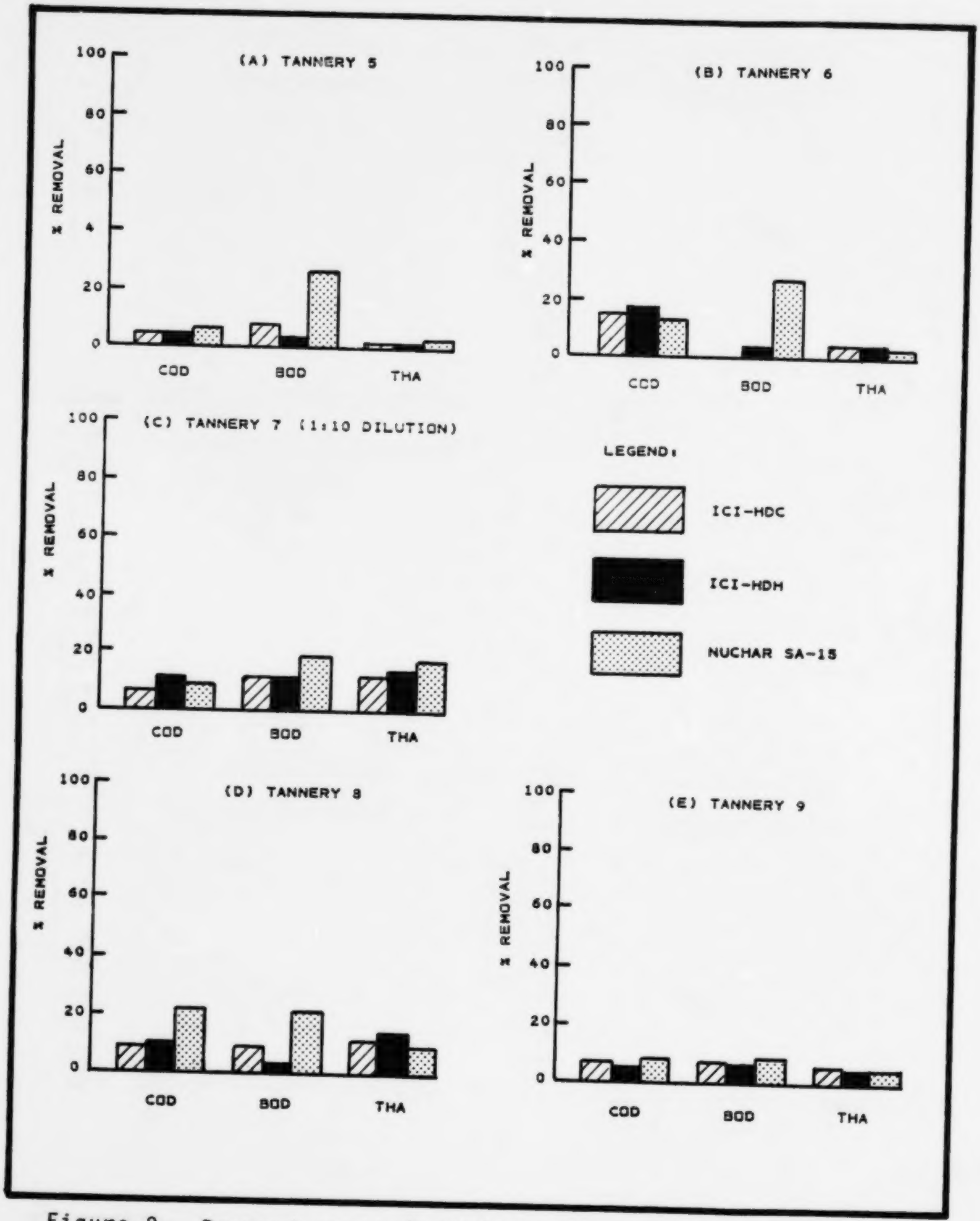

Figure 2. Percent removal of COD, BOD, and THA from Tanneries 5 through 9 effluents using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons at 0.3 g/l dose.

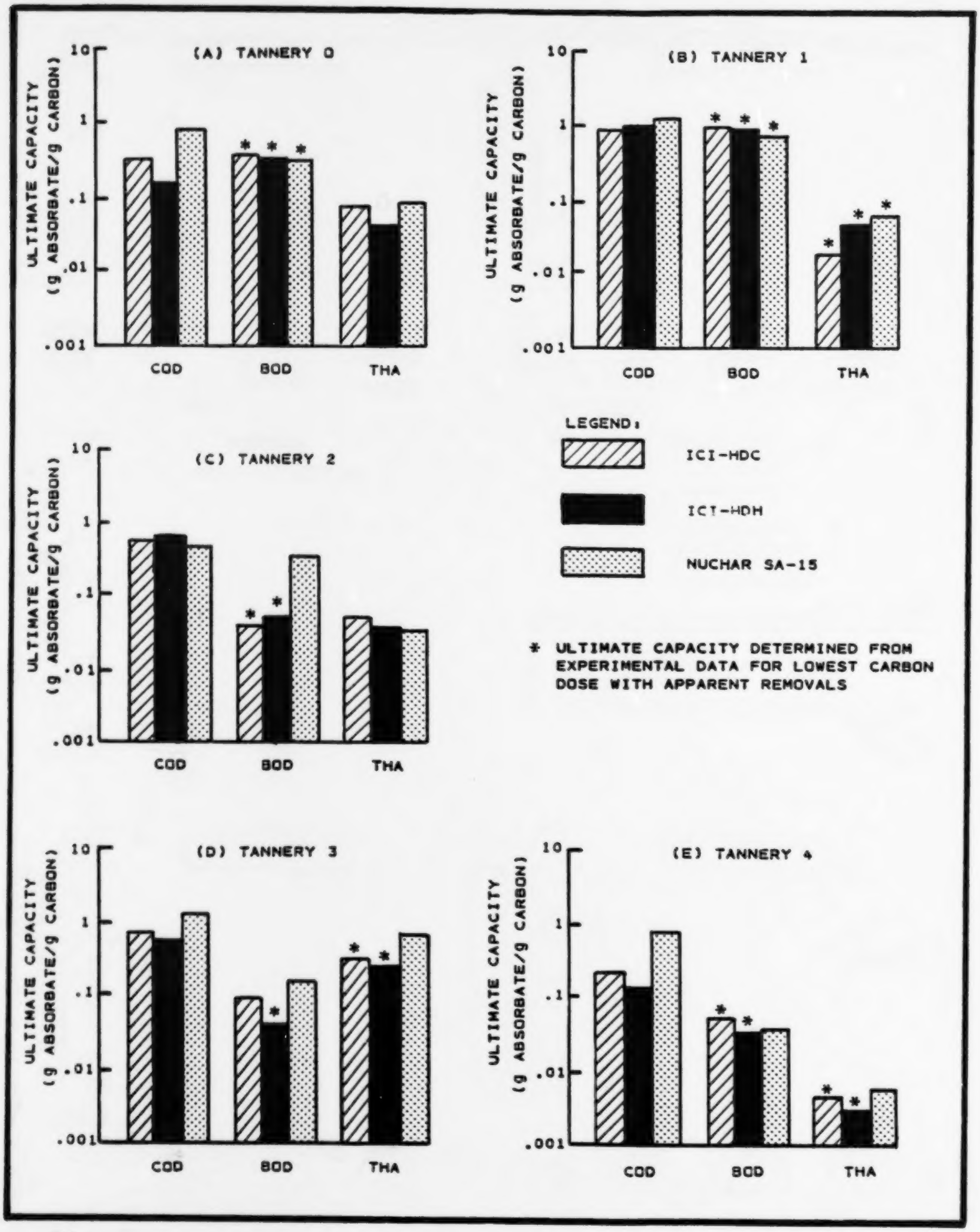

Figure 3. Ultimate capacities of ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons for removal of COD, BOD, and THA from Tanneries 0 through 4 effluents.

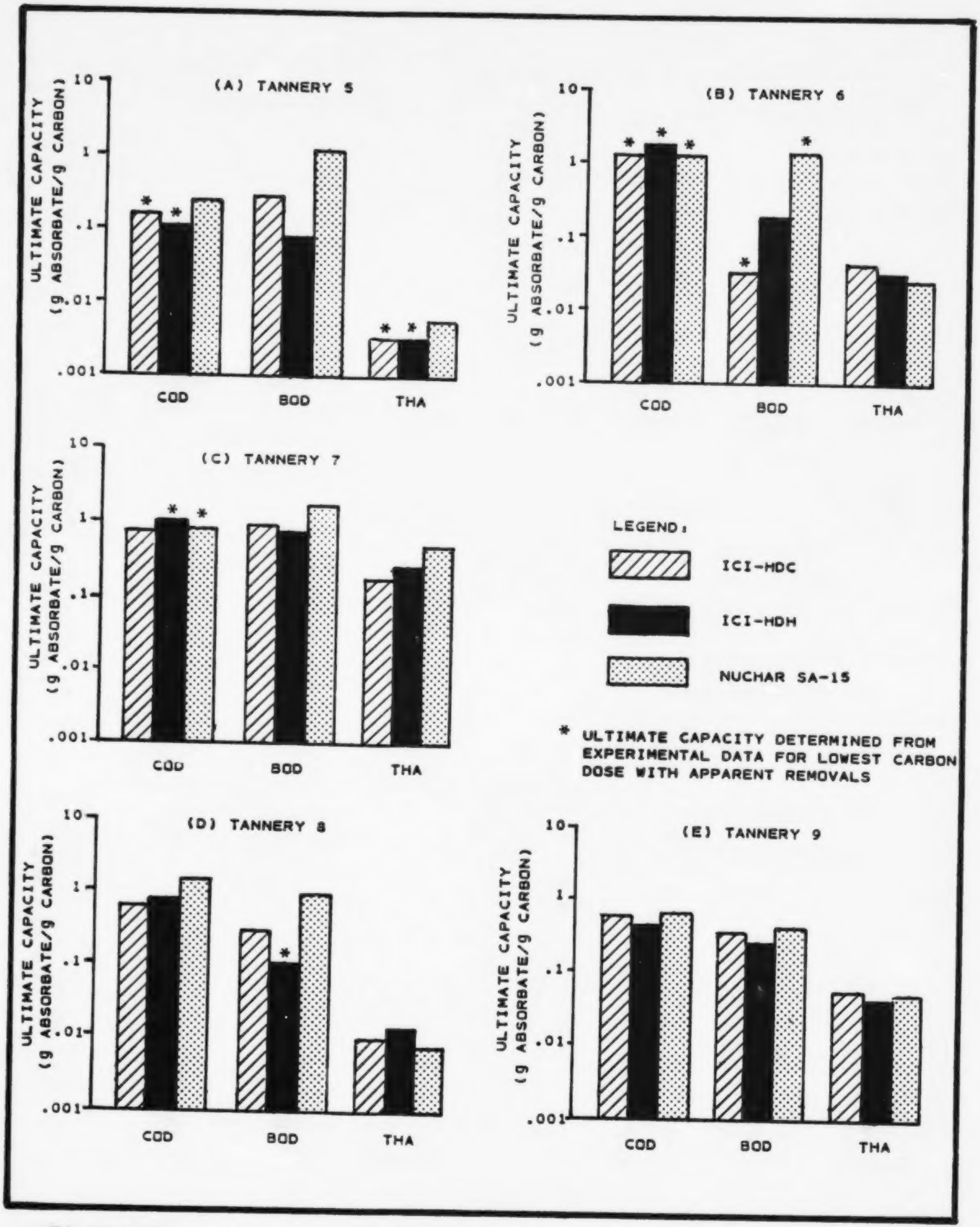

Figure 4. Ultimate capacities of ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons for removal of COD, BOD, and THA from Tanneries 5 through 9 effluents.

For Tannery 1 effluent, ultimate capacities of all three carbons for the removal of COD were found to range from approximately 0.9 to 1.3 g COD/g carbon, while those for BOD ranged from 0.75 to 1 g BOD/g carbon. Ultimate capacities for the removal of THA compounds, however, were estimated to be lower, ranging from 0.02 to 0.06 g THA/g carbon.

For Tannery 2 effluent, the ICI carbons were found to be more efficient for COD removal than Nuchar SA-15, with ultimate capacities of approximately 0.6 and 0.45 g COD/g carbon, respectively. In terms of BOD removal, however, ICI carbons were found to be ineffective for this particular effluent, with ultimate capacities ranging from 0.04 to 0.05 g BOD/g carbon; Nuchar SA-15 exhibited an ultimate capacity of 0.4 g BOD/g carbon. Ultimate capacities of all three carbons for THA removal were estimated to be approximately 0.04 to 0.05 g THA/g carbon.

In the treatment of Tannery 3 effluent, Nuchar SA-15 exhibited the highest ultimate COD removals (1.2 g COD/g carbon), while those of both ICI carbons were estimated to be approximately 0.6 g COD/g carbon. For BOD removal from this effluent, the experimental data indicated the following ultimate capacities: ICI-HDC, 0.09; ICI-HDH, 0.04; and Nuchar SA-15, 0.16 g BOD/g carbon. Ultimate capacities of all three carbons for THA removal were approximately 0.3 to 0.4 g THA/g carbon.

At Tannery 4, the highest ultimate capacity for the removal of COD was exhibited by Nuchar SA-15 (1 g COD/g carbon), followed by the two ICI carbons (0.15 to 0.25 g COD/g carbon). Ultimate capacities for BOD removal were estimated to be higher for ICI-HDC and Nuchar SA-15 (0.05 to 0.04 g BOD/g carbon, respectively) than for ICI-HDH (less than 0.02 g BOD/g carbon). All three carbons were found to be quite ineffective for THA removal; their ultimate capacities ranged from 0.003 to 0.006 g THA/g carbon.

Tests with Tannery 5 effluent revealed that Nuchar SA-15 had a slightly higher capacity (0.35 g COD/g carbon) for the removal of COD-contributing compounds than the ICI carbons (0.1 to 0.2 g COD/g carbon). In terms of BOD removal, the ultimate capacity of Nuchar SA-15 was estimated to be approximately 1 g BOD/g carbon; those of ICI-HDC and ICI-HDH were 0.3 and 0.07 g BOD/g carbon, respectively. The ultimate capacities of all three carbons for THA removal were found to be approximately 0.003 to 0.005 g THA/g carbon.

Ultimate capacities of the carbons for the removal of COD from Tannery 6 effluent were estimated to be approximately 0.16 (ICI-HDC), 0.1 (ICI-HDH), and 0.35 g COD/g carbon (Nuchar SA-15). For BOD removal, ICI-HDC was found to be essentially ineffective with an estimated ultimate capacity of less than 0.03 g BOD/g carbon. The ultimate capacity of ICI-HDH was found to be 0.2 g BOD/g carbon, and that of Nuchar SA-15 was approximately an order of magnitude higher. Ultimate capacities of all three carbons for the removal of THA from this particular effluent were estimated to be in the range of 0.03 to 0.04 g THA/g carbon.

The ultimate capacities of the three carbons for the removal of COD from 1:10 dilution of Tannery 7 effluent were estimated to be as follows: ICI-HDC, 0.8 g COD/g carbon; ICI-HDH, 1 g COD/g carbon; and Nuchar SA-15, 0.9 g COD/g carbon. Ultimate capacities of all three carbons for BOD removal from the same dilution of Tannery 7 effluent were found to be approximately 1 g BOD/g carbon; those for THA removal ranged from 0.2 to 0.5 g THA/g carbon.

At Tannery 8, the experimental data revealed that the ultimate capacities of all three carbons for COD removal ranged from 0.7 to 1.4 g COD/g carbon; those for BOD removal ranged from 0.09 to 0.9 g BOD/g carbon. Saturation capacities of all three carbons for THA removal were approximately 0.01 g THA/g carbon.

For Tannery 9 effluent, the experimental data yielded approximate ultimate capacities of 0.4 to 0.5 g COD/g carbon for all three carbons. Those for BOD removal were in the range of 0.3 to 0.4 g BOD/g carbon, while those for THA were estimated to be approximately 0.5 g THA/g carbon.

It can be generally concluded that within Tanneries 0, 2, 3, 7, and 9, all three carbons exhibited differences in ultimate capacities equal to or less than one order of magnitude; for Tanneries 1, 4, 5, 6, and 8, differences between ultimate capacities were found to be greater than one order of magnitude.

The above observations indicate that the removals of COD, BOD, and THA were a function of carbon type and/or effluent characteristics; differences in removals may be attributed to factors such as effluent composition, speciation, total concentration of sorbates, competition of sorbates for the available adsorption sites, and carbon surface characteristics. The specific reasons for these differences cannot be determined at the present time.

SPECIFIC PHENOLS

Four specific chlorophenols were considered in these investigations: pentachlorophenol, 2,4,5-trichlorophenol, tetrachlorophenol, and 2,4-dichlorophenol. Their presence and removal by PAC sorption were examined for Tannery 5 and 7 effluents only. All three carbons essentially removed most of the identified specific phenols from Tannery 5 effluent, but had no observable effect on the effluent from Tannery 7.

TOC

Accountable decreases in TOC concentrations were observed only at high carbon doses, indicating low efficiencies of all three carbons for the removal of TOC from all effluents tested.

CHROMIUM

Interpretation of the chromium results was not possible due to the lack of available information on both chemical speciation of chromium and detailed chemical characterization of the respective effluents.

OIL AND GREASE

All of the PAC's tested were essentially ineffective with respect to oil and grease removals.

COST ESTIMATES

The daily cost for PAC addition at doses of 300 mg/l to an existing biological treatment system at an assumed flow rate of 100,000 gal/day was estimated to be approximately $125 per day. Higher carbon doses (10 g/l) would increase daily costs up to $4,250 (for carbon only).

SUMMARY

Comparison of the raw wastewater characteristics of the four pairs of tanneries within the same subcategory indicated no similarities in the concentration of wastewater constituents (Table 1). Analysis of the adsorption data indicated that the PAC's have limited ability to bind COD, BOD, TOC, THA, chromium, and oil and grease in tannery effluents (see Tables 2, 3, and 4). Furthermore, there was no apparent correlation between final effluent characteristics and the nature of the tanning operations.

TABLE 1. CHEMICAL CHARACTERISTICS OF TANNERY EFFLUENTS

Tannery Subcategory	Tannery Number	Concentration* (mg/l)					
		COD	BOD	THA†	TOC	Total Chromium	Oil and Grease
1	1	2,370	1,380	179	640	5.4	46
	4	854	574	49.6	375	3.75	94
2	5	1,190	590	55	340	2.8	110
3	6	3,470	1,920	212	750	-	68
	9	2,280	1,300	255	730	1.92	48
4	0	410	228	27.3	182	0.86	60
	2	1,190	738	63.8	475	1.6	38
5	3	2,090	988	120	820	12.1	24
6	7#	2,770	1,620	325	275	30.9	1,120
	8	2,160	1,050	26.5	570	1.86	42

* Determined on aerated samples.

† Total hydroxylated aromatics expressed as phenol.

# Corresponds to 1:10 dilution of Tannery 7 effluent.

TABLE 2. PERCENT REMOVALS OF TANNERY EFFLUENT CONSTITUENTS† AT 0.3 g/l PAC

Tannery Subcategory	Tannery Number	COD*			BOD*			THA*,††			TOC##			Total Chromium##			Oil and Grease##		
		ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15
1	1	8	14	14	3	5	5	20	15	22	38	35	2	4	-	-	-	-	48
	4	7	5	19	2	2	3	3	0	2	20	17	25	-	41	7	19	2	-
2	5	5	3	7	21	16	15	10	3	27	18	1	12	79	39	86	69	80	55
3	6	15	17	13	5	4	4	0	3	27	-	1	7	-	-	-	65	41	59
	9	7	5	7	6	5	6	7	6	8	1	1	4	40	-	54	33	33	33
4	0	18	10	36	39	30	50	48	43	30	5	5	34	36	15	65	57	47	77
	2	13	13	10	21	16	15	2	1	12	11	26	1	19	-	13	-	11	21
5	3	8	7	16	63	68	35	3	1	4	5	16	34	9	-	-	-	-	17
6	7#	6	11	8	12	13	17	11	11	18	5	13	15	19	33	86	-	-	38
	8	9	9	24	11	14	9	8	3	21	12	12	21	2	-	-	38	33	43

* Determined using lines of best fit.

† Specific phenolic compounds excluded due to inconclusive data.

Corresponds to 1:10 dilution of Tannery 7 effluent.

†† Total hydroxylated aromatics expressed as phenol.

Corresponds to experimental points.

TABLE 3. PERCENT REMOVALS OF TANNERY EFFLUENT CONSTITUENTS† AT 0.6 g/1 PAC

Tannery Subcategory	Tannery Number	COD*			BOD*			THA*,††			TOC##			Total Chromium##			Oil and Grease##		
		ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15
1	1	13	23	23	28	22	29	5	9	8	38	41	11	11	48	-	-	13	-
	4	13	9	29	5	0	4	4	4	7	13	18	9	-	49	7	11	-	17
2	5	8	6	12	3	3	20	4	4	6	21	3	15	71	64	88	73	78	55
3	6	24	23	20	0	5	42	10	8	7	4	3	16	-	-	-	71	38	44
	9	12	10	14	13	10	14	12	10	11	1	7	4	30	-	29	46	29	29
4	0	29	18	45	58	52	39	45	66	38	34	-	45	54	21	71	20	57	37
	2	23	23	17	3	3	20	37	27	27	11	26	26	25	-	-	-	11	32
5	3	14	12	24	17	6	36	73	74	46	12	5	20	-	-	-	17	17	17
6	7#	10	14	12	17	17	26	19	20	24	9	11	5	-	27	88	25	14	27
	8	16	18	39	16	6	35	20	25	17	21	16	47	1	-	19	33	19	33

* Determined using lines of best fit.

† Specific phenolic compounds excluded due to inconclusive data.

# Corresponds to 1:10 dilution of Tannery 7 effluent.

†† Total hydroxylated aromatics expressed as phenol.

## Corresponds to experimental points.

TABLE 4. PERCENT REMOVALS OF TANNERY EFFLUENT CONSTITUENTS† AT 1.5 g/l PAC

Tannery Subcategory	Tannery Number	COD*			BOD*			THA*,††			TOC##			Total Chromium##			Oil and Grease##		
		ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15	ICI-HDC	ICI-HDH	Nuchar SA-15
1	1	22	37	37	40	33	38	12	17	17	37	45	66	-	35	2	30	43	-
	4	24	19	44	13	0	10	9	9	15	31	25	43	-	31	9	23	1	81
2	5	18	14	21	28	15	49	9	9	14	25	18	35	87	75	65	69	82	46
3	6	37	33	32	0	11	63	21	16	18	13	20	13	-	-	-	50	65	15
	9	25	20	28	25	20	27	26	20	25	14	9	22	100	-	61	33	29	42
4	0	47	55	49	70	62	50	68	64	83	65	24	36	56	94	73	73	63	57
	2	43	41	32	8	7	36	63	49	48	11	26	47	19	31	19	5	-	53
5	3	26	24	36	10	5	13	83	81	58	34	29	1	15	50	-	25	33	33
6	7#	18	19	17	26	28	39	30	31	32	27	5	27	33	45	96	7	7	20
	8	32	39	63	33	15	58	44	50	37	47	30	81	1	2	-	24	10	24

* Determined using lines of best fit.

† Specific phenolic compounds excluded due to inconclusive data.

# Corresponds to 1:10 dilution of Tannery 7 effluent.

†† Total hydroxylated aromatics expressed as phenol.

## Corresponds to experimental points.

SECTION 3

RECOMMENDATIONS

Based on the results of this study, the following recommendations are given:

1. Any future related PAC research efforts should be conducted on an effluent-by-effluent basis.
2. The relationship between PAC dosages and different specific phenols needs to be further investigated.

SECTION 4

SAMPLING, EXPERIMENTAL, AND ANALYTICAL PROCEDURES

This section provides the reader with a detailed description of sampling, experimental, and analytical procedures, and isotherm calculations.

SAMPLING PROCEDURES

Effluent samples were collected from 10 tanneries representing six of the seven tanning subcategories classified by EPA-EGD (see Appendix C). Grab samples were taken periodically throughout a typical operating day (8 to 16 hours) to provide approximately 120 l of raw, untreated effluent (except as noted below).

Samples were obtained from a point within each plant that best represented a combined raw waste load. Typically, these points were equalization basins, sumps, or ends-of-pipe. At two tanneries, two individual split streams were sampled, and later combined in the laboratory. It was not possible to sample the combined waste stream from Tannery 4 at any point other than the neutralization tank after pretreatment. Sampling points for each tannery are shown in Table 5 below.

Approximately 100 l of samples from each tannery were collected in acid-washed 4-l cubitainers. An additional 20 l from each tannery were collected in 4-l amber glass jars, previously rinsed with spectrophotometric-grade methylene chloride. All samples were placed in freezer storage for a minimum of 24 hours prior to shipment to the laboratory.

The frozen samples were packed in Styrofoam-lined cardboard boxes. Frozen "blue" ice containers were added to all boxes to maintain 0°C conditions during shipment. Samples were airfreighted to Los Angeles, and immediately transferred to laboratory freezer storage (approximately -20°C). All samples were received either partially or completely frozen.

TABLE 5. SAMPLING LOCATIONS AT 10 LEATHER TANNING PLANTS

Tannery No.	Subcategory*	Sampling Point
0	4	Holding tank prior to discharge to POTW
1	1	Separate end-of-pipe samples from tanhouse and beamhouse operations
2	4	Equalization tank
3	5	Combined sample from final washing and neutralization tank
4	1	Neutralization tank after pretreatment
5	2	Equalization basin
6	3	Sump prior to primary clarifier
7	6	Equalization basin
8	6	Equalization basin
9	3	Collection basin after screening

* EPA Designations (1).

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Chemicals and Glassware

All of the chemical reagents used in this research were Analytical Reagent Grade. All solutions were made with deionized water obtained by passing tap water through a Culligan Uni-Bed ion-exchange column. All glassware was cleaned with Alconox detergent and triple-rinsed with distilled water.

PAC's

Six PAC's were used to develop adsorption isotherms. These were:

PAC Designation	Manufacturer
Amoco PX-21	Amoco Research Corporation
Westates WO-841	Westates Carbon
Norit FQA	American Norit Company

Nuchar SA-15	Westvaco
Hydrodarco C (ICI-HDC)	ICI Americas, Inc.
Hydrodarco H (ICI-HDH)	ICI Americas, Inc.

Each of the above PAC's were evaluated at Tanneries 0 and 4. Based on those isotherm results and commercial availability, ICI-HDC, ICI-HDH, and Nuchar SA-15 were evaluated on the eight remaining effluents. Table 6 below presents comparative data on each of the PAC's.

TABLE 6. PHYSICAL AND CHEMICAL PROPERTIES OF SIX PAC'S

Property	Amoco PX-21	ICI-HDC	ICI-HDH	Nuchar SA-15	Norit FOA	Westates WO-841
Surface Area (m^2/g)	2,800-3,500	550	475	1,400-1,800	600	700
Iodine No.	2,800-3,600	NA*	NA	800	750	550
Bulk Density (g/cc)	0.27-0.32	0.7	0.7	0.7	0.4	NA
Particle Size						
%-100 Mesh	90-99	NA	NA	95-100	95-100	100
%-200 Mesh	70-85	NA	NA	85-95	80-85	97
%-325 Mesh	55-70	70	NA	65-85	60-65	90
pH	7-9	10.5	10.5	3-6	9-11	11

* NA = Not Available.

pH Determinations

Determinations of pH were carried out using an Orion pH meter (Model 701) and an Orion Combination Model 91-05 pH electrode.

COD Determinations

COD determinations were carried out using the EPA-approved ampule technique, as per method by Oceanography International Corporation. A detailed description of this method is offered in Appendix B.

BOD Determinations

The BOD concentrations were determined by the method outlined in Standard Methods (2).

THA Determinations

Determinations of THA (expressed as total phenol) were obtained using the modified Lowry procedure (Folin-Ciocalteau) of Markwell, et al. (3). Details of this method are provided in Appendix B.

Oil and Grease Determinations

Oil and grease concentrations were determined by the method outlined in the EPA Methods for Chemical Analysis of Water and Wastes (4).

Total Chromium Determinations

Total chromium determinations were made in accordance with Standard Methods (2). A Perkin-Elmer Model 280 atomic absorption spectrophotometer was used for all chromium determinations.

TOC Determinations

TOC determinations were made with a Beckman Model 915 TOC analyzer in accordance with the manufacturer's instructions.

Determinations of Specific Phenols

Samples were acidified with H_2SO_4 and extracted with benzene in the ratio of 10:1. Analysis was performed using a Fisher Model 2400 gas chromatograph with Supelcoport 80/100 mesh, coated with 1 percent SP-1240DA. An electron capture detector was used. Details of this method are provided in Appendix B.

Experimental Procedures

Frozen samples from each tannery were removed and allowed to equilibrate to room temperature prior to testing. The contents from all cubitainers from any one tannery were combined in a large plastic container, and stirred gently for 10 minutes to effect homogeneity. The cubitainers were carefully washed with deionized water, and were refilled with the composited sample. Sufficient aliquot was withdrawn for adsorption experiments; the remaining cubitainers were returned to the freezer for retention and subsequent analysis.

Bench-scale adsorption experiments utilized the following equipment:

- Magnetic stirrer.
- 2-l beaker.
- Teflon-coated magnetic stir bar.
- Watch glass (placed over the beaker during stirring to contain splashing).

Seven 2-l bench-scale aeration units were used for each PAC tested on any individual tannery effluent. One l of the effluent was placed into each of the bench-scale units. To each of the first six units, 300, 600, 900, 1,200, 1,500, and 10,000 mg/l doses of PAC were added, respectively. No PAC was added to the seventh unit; this served as an aerated control.

The effluent-PAC slurry was allowed to stir for 1 hour at room temperature (22° ± 2°C) at 1,000 rpm, creating a vortex through which the bottom of the unit was visible. The ambient pH values for all experiments are given in Appendix A, Table A-13. The slurry was filtered immediately through a Buchner funnel using Whatman No. 40 filter paper. Prior to placing the sample into a previously cleaned 1-l polyethylene bottle, the pH of the filtrate was recorded. One hundred ml were set aside for BOD analysis (started on the same day as filtration). The remaining 900 ml were acidified to pH <2 with H_2SO_4, if sulfides were found to be absent. Acidification of sulfide-containing effluents liberated H_2S and coagulated much of the proteinaceous material, which subsequently interfered with chemical analysis. Sulfide-containing effluents were either analyzed immediately or were kept chilled (4°C) prior to analysis.

The individual sample fractions from each effluent for each PAC dosage were analyzed for BOD, COD, TOC, pH, oil and grease, THA (expressed as total phenol), and total chromium.

In addition to the above, effluents from Tanneries 5 and 7, stored in glass, were reacted with Nuchar SA-15, ICI-HDC, and ICI-HDH, respectively, to determine the effectiveness of removing four specific phenols: pentachlorophenol, 2,4,5-trichlorophenol, tetrachlorophenol, and 2,4-dichlorophenol.

FREUNDLICH ISOTHERM CALCULATIONS

The adsorption isotherm is the relationship, at a given temperature, between the amount of a substance adsorbed and its surrounding solution, as expressed by the Freundlich equation:

$$x/m = kC^{1/n} \qquad (1)$$

where

x = amount of constituent adsorbed

m = weight of carbon dose

x/m = amount of constituent adsorbed per unit weight of carbon dose

k&n = constants

C = unadsorbed concentration of constituent remaining in solution.

In logarithmic form, this equation is:

$$\log x/m = \log k + 1/n \log C \qquad (2)$$

in which $1/n$ represents the slope of the straight line isotherm whose intercept at $C=1$ yields the equilibrium constant K. Isotherms obey the Freundlich equation if x/m plotted against C on log-log paper results in a straight line.

Ultimate Capacity Calculation

Lines of best fit through the experimental data (provided in Appendix A, Tables A-1 through A-12) were obtained by performing a least squares linear regression using Equation 2 by substituting $1/n$ and k values for each data set. These lines were subsequently used in the determination of ultimate capacities.

Ultimate capacity is the theoretical weight of constituent adsorbed per unit weight of carbon when the carbon is in equilibrium with the surrounding solution. Its value can be found graphically by extrapolating a line of best fit to intersect a vertical line corresponding to the influent concentration (C_0). The expression for ultimate capacity is the Freundlich equation (Equation 1) with $C = C_0$:

$$(x/m)C_0 = kC_0{}^{1/n} \qquad (3)$$

where

C_0 = initial concentration of sorbate

Percent Adsorption Calculations

To obtain percent adsorption from the lines of best fit for different sorbates at a given carbon dose, the Freundlich equation was rearranged to yield a nonlinear expression for constituent concentrations:

$$x = (C_0 - C)/1{,}000 \qquad (4)$$

where

C_o = initial concentration of constituent in solution, mg/l

C = unadsorbed concentration of constituent remaining in solution, mg/l

x = amount of constituent adsorbed, g/l

Then, substituting x in Equation 1 with Equation 4 yields

$$(C_o-C)/(1{,}000m) = kC^{1/n} \tag{5}$$

$$1{,}000mkC^{1/n} + C-C_o = 0 \tag{6}$$

Since the procedure for calculating the concentration is fairly complex, and numerous calculations were required, a computer program was used to provide the required answers. The method known as a flexible polyhedron search (5) was selected solely on the ready availability of the required software.

SECTION 5

RESULTS AND DISCUSSION

INTRODUCTION

In the discussion that follows, the effectiveness of carbon adsorption in the removal of selected pollutants from tannery effluents was examined. Comparisons between the individual carbons were performed in terms of removal efficiencies and carbon saturation capacities. It should be noted that adsorption isotherms were not developed for cases where either (1) saturation capacities were reached or were approached within most of the carbon dose ranges investigated, or (2) the correlation coefficient for the data was <0.70. In these cases, ultimate capacities were assumed to be those calculated from experimental data for the lowest carbon dose that exhibited apparent removals.

COD

Tannery 0

COD is one of the parameters most suitable for determining removal efficiencies of organic substances from tannery wastewaters. Figures 5 and 6 show log-log plots of equilibrium data for the sorption of COD-contributing compounds from Tannery 0 effluent (shown in Tables A-1 and A-2). The data for the six carbons tested showed conformance to the empirical Freundlich adsorption isotherm. From an inspection of these isotherms, it was concluded that COD removals could be accomplished by all six carbons. However, more detailed analysis of Figures 5 and 6, in conjunction with Table 7, revealed that for an initial COD concentration of 410 mg/l, the presence of 0.3 g/l PAC resulted in 18 percent COD removal with ICI-HDC, 10 percent with ICI-HDH, 36 percent with Nuchar SA-15, and 20, 6, and 33 percent COD removal using Norit FQA, Westates WO-841, and Amoco PX-21, respectively (Table 7). An increase in PAC doses from 0.3 to 1.5 g/l resulted in the following increases in COD removal: approximately 29 percent using ICI-HDC and Norit carbons; 25 percent for Amoco PX-21; and 24, 19, and 17 percent for ICI-HDH, Nuchar SA-15, and Westates WO-841, respectively. At 1.5 g/l, COD removals were 57 and 55 percent (Amoco PX-21 and Nuchar SA-15, respectively), 49 and 47 percent (Norit FQA and ICI-HDC, respectively), and 34 and 23 percent (ICI-HDH and Westates WO-841, respectively). Adsorption isotherm plots (Figures 5 and 6) revealed that the ultimate amount of adsorbable COD-contributing constituents in Tannery 0 effluents (initial concentration of 410 mg/l) was apparently the

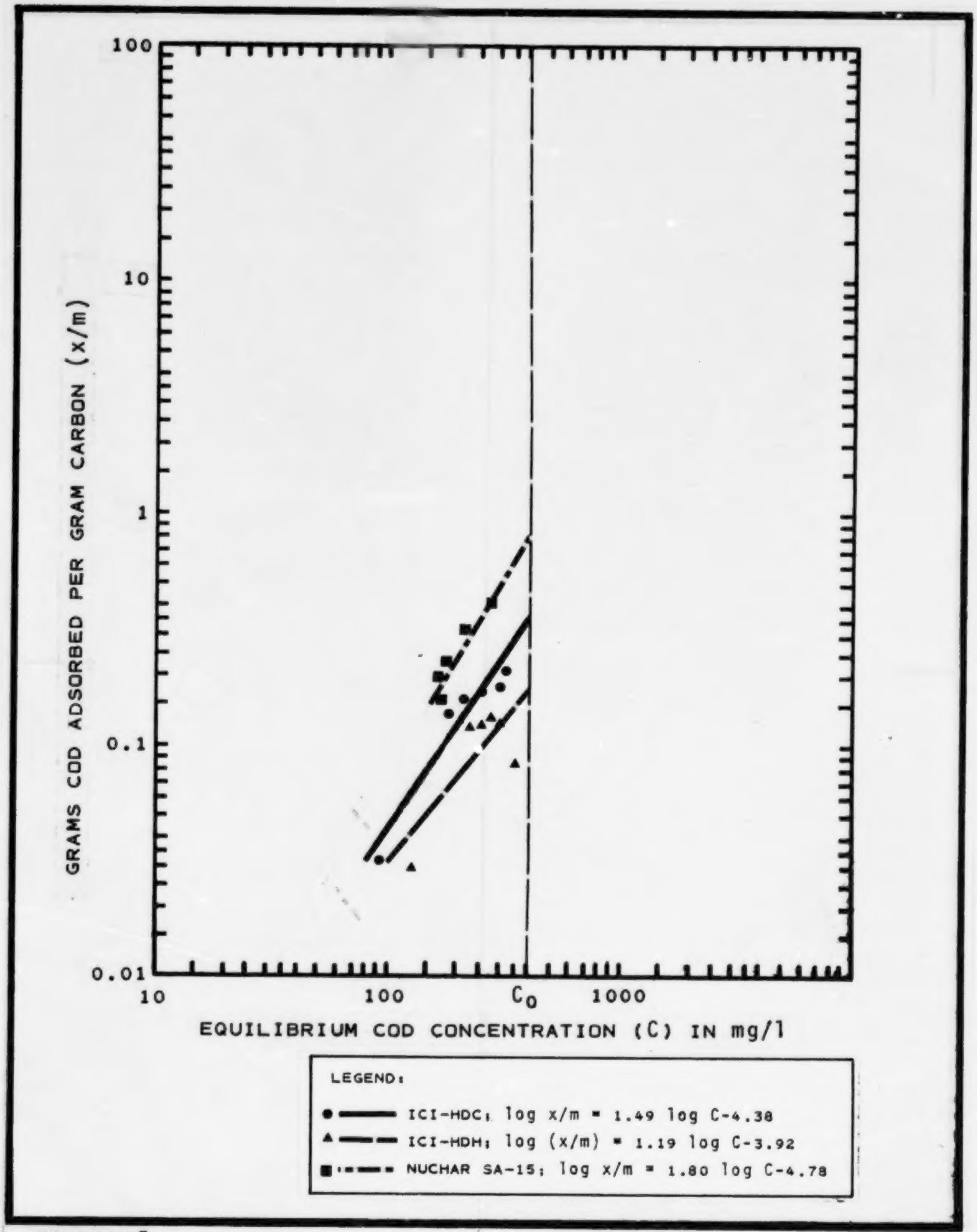

Figure 5. Freundlich adsorption isotherms for COD removal from Tannery O effluent (C_0 = 410 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

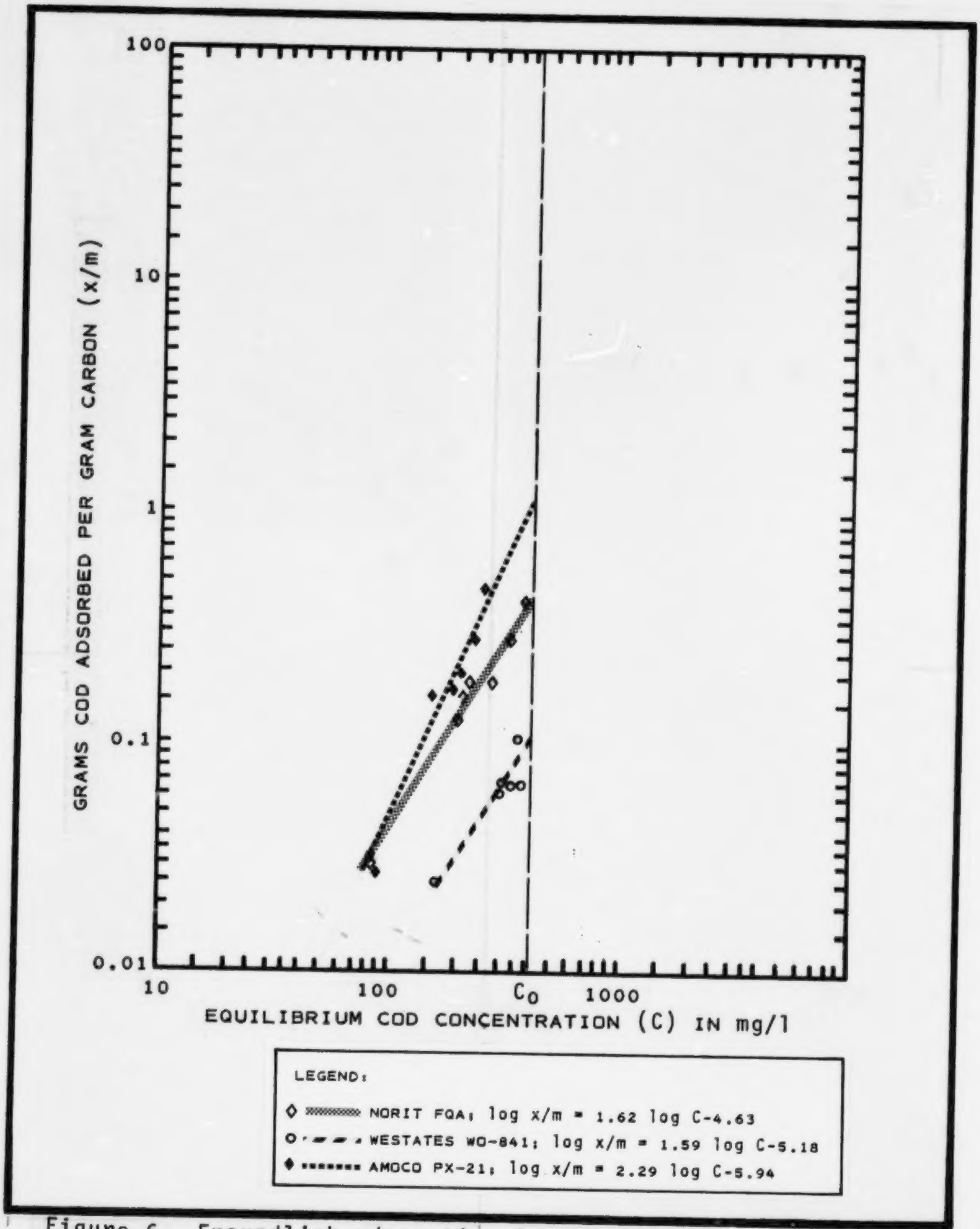

Figure 6. Freundlich adsorption isotherms for COD removal from Tannery O effluent (C_0 = 410 mg/l) using Norit FQA, Westates WO-841, and Amoco PX-21 carbons.

TABLE 7. PERCENT COD REMOVAL AS A FUNCTION OF CARBON DOSE*

		Carbon Dose (g/l)																	
	Initial Concentration	0.3						0.6						1.5					
Tannery	(mg/l)	HDC	HDH	NUCH	NOR	WEST	AMO	HDC	HDH	NUCH	NOR	WEST	AMO	HDC	HDH	NUCH	NOR	WEST	AMO
0	410	17.8	10.0	36.1	20.3	6.2	32.7	28.8	17.9	44.5	31.7	11.4	43.6	46.5	34.3	54.9	49.1	22.8	57.4
1	2,366	8.2	14.0	14.4	-	-	-	13.2	22.6	22.8	-	-	-	21.9	36.9	36.5	-	-	-
2	1,188	13.1	13.4	9.7	-	-	-	23.1	23.1	17.1	-	-	-	42.5	41.1	32.1	-	-	-
3	2,089	8.2	6.9	15.6	-	-	-	14.3	12.4	23.5	-	-	-	26.4	23.9	35.7	-	-	-
4	854	7.0	4.7	19.4	2.0	0	25.8	12.5	8.9	29.3	3.9	0	34.3	23.9	19.1	44.1	9.4	0	45.6
5	1,188	4.5	3.4	7.0	-	-	-	8.4	6.4	11.8	-	-	-	18.0	14.2	20.7	-	-	-
6	3,465	15.2	16.7	12.7	-	-	-	23.6	23.3	20.1	-	-	-	36.8	32.8	32.2	-	-	-
7	2,772†	5.5	10.8	7.9	-	-	-	9.6	14.0	11.5	-	-	-	17.6	18.6	17.2	-	-	-
8	2,158	8.5	9.3	23.5	-	-	-	15.8	17.7	38.8	-	-	-	32.2	38.7	62.8	-	-	-
9	2,277	6.6	5.3	7.4	-	-	-	12.3	9.7	13.7	-	-	-	25.1	19.6	27.8	-	-	-

* HDC = ICI-HDC
HDH = ICI-HDH
NUCH = Nuchar SA-15
NOR = Norit FQA
WEST = Westates WO-841
AMO = Amoco PX-21.

† Corresponds to 1:10 dilution of the original sample.

highest for Amoco PX-21 and Nuchar SA-15 (1.1 and 0.8 g COD/g carbon, respectively), followed by Norit FQA and ICI-HDC (0.3 to 0.4 g COD/g carbon); ultimate capacities of the two remaining carbons ranged from approximately 0.09 g COD/g carbon (Westates WO-841) to 0.15 g COD/g carbon (ICI-HDH).

Tannery 4

Effluent from Tannery 4 was characterized by 850 mg/l COD. Equilibration of this effluent with different doses of Nuchar SA-15 and Amoco PX-21 carbons, ranging from 0.3 to 1.5 g/l, resulted in 19 to 44 percent and 25 to 46 percent COD removal, respectively (Table 7). Equilibration with ICI-HDC and ICI-HDH carbons resulted in 7 and 5 percent COD removals, respectively, at doses of 0.3 g/l, and in 24 and 19 percent COD removals at doses of 1.5 g/l. Norit FQA removed only 2 to 9 percent COD from Tannery 4 effluent in the same dose range, while Westates WO-841 was completely ineffective.

From the adsorption isotherms presented in Figures 7 and 8, the ultimate capacities of the five effective carbons were found to be in the range of 0.06 to 2 g COD/g carbon. The two best carbons appeared to be Amoco PX-21 and Nuchar SA-15, followed by ICI-HDC, and ICI-HDH.

Tannery 1

A 0.3 g/l dose of Nuchar SA-15, ICI-HDC, and ICI-HDH carbons, when applied to Tannery 1 effluent (characterized by COD concentrations of 2,370 mg/l), were found to be effective in removing 14, 8, and 14 percent COD, respectively (see Table 7). A fivefold increase in the carbon dose resulted in 19, 29, and 24 percent increases in COD removal by the above respective carbons. Adsorption isotherms (Figure 9) and analysis of the data presented in Table A-5 indicated similar ultimate capacities for all three carbons, ranging from approximately 0.9 to 1.3 g COD/g carbon, with Nuchar SA-15 being the highest.

Tannery 9

At 0.3 g/l, Nuchar SA-15 appeared to be the most efficient of the carbons, resulting in approximately 7 percent COD removal (Table 7). The apparent COD removals by ICI-HDC and ICI-HDH carbons amounted to only 7 and 5 percent, respectively. At 1.5 g/l carbon doses, these COD removals were increased an additional 14 to 20 percent. The experimental data, plotted in the form of Freundlich adsorption isotherms, yielded approximate ultimate capacities of 0.4 to 0.5 g COD/g carbon for all three carbons (Figure 10).

Tannery 6

Equilibration of the Tannery 6 effluent with 0.3 g/l of each carbon resulted in only 13 to 17 percent COD removals, while a

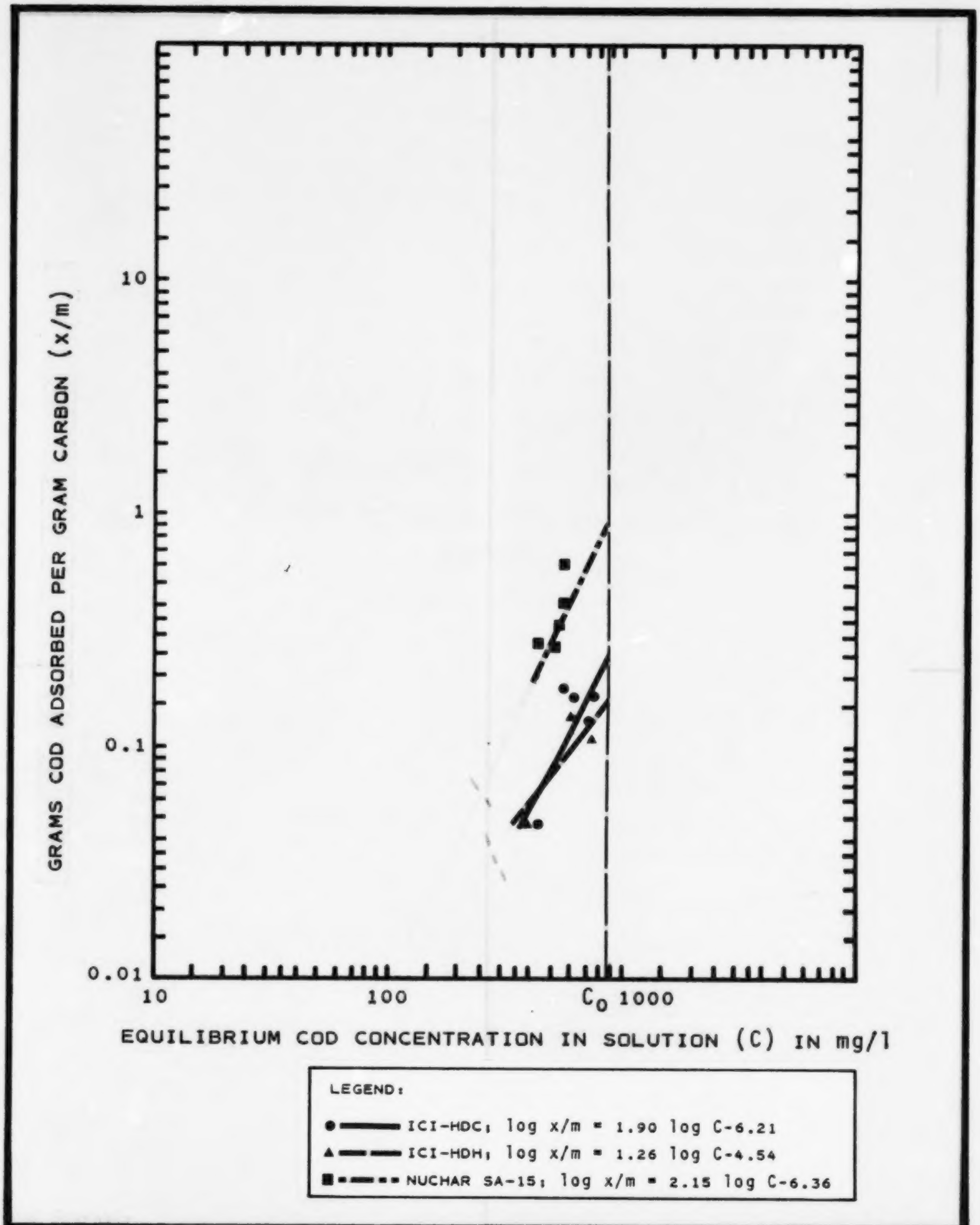

Figure 7. Freundlich adsorption isotherms for COD removal from Tannery 4 effluent (C_0 = 854 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

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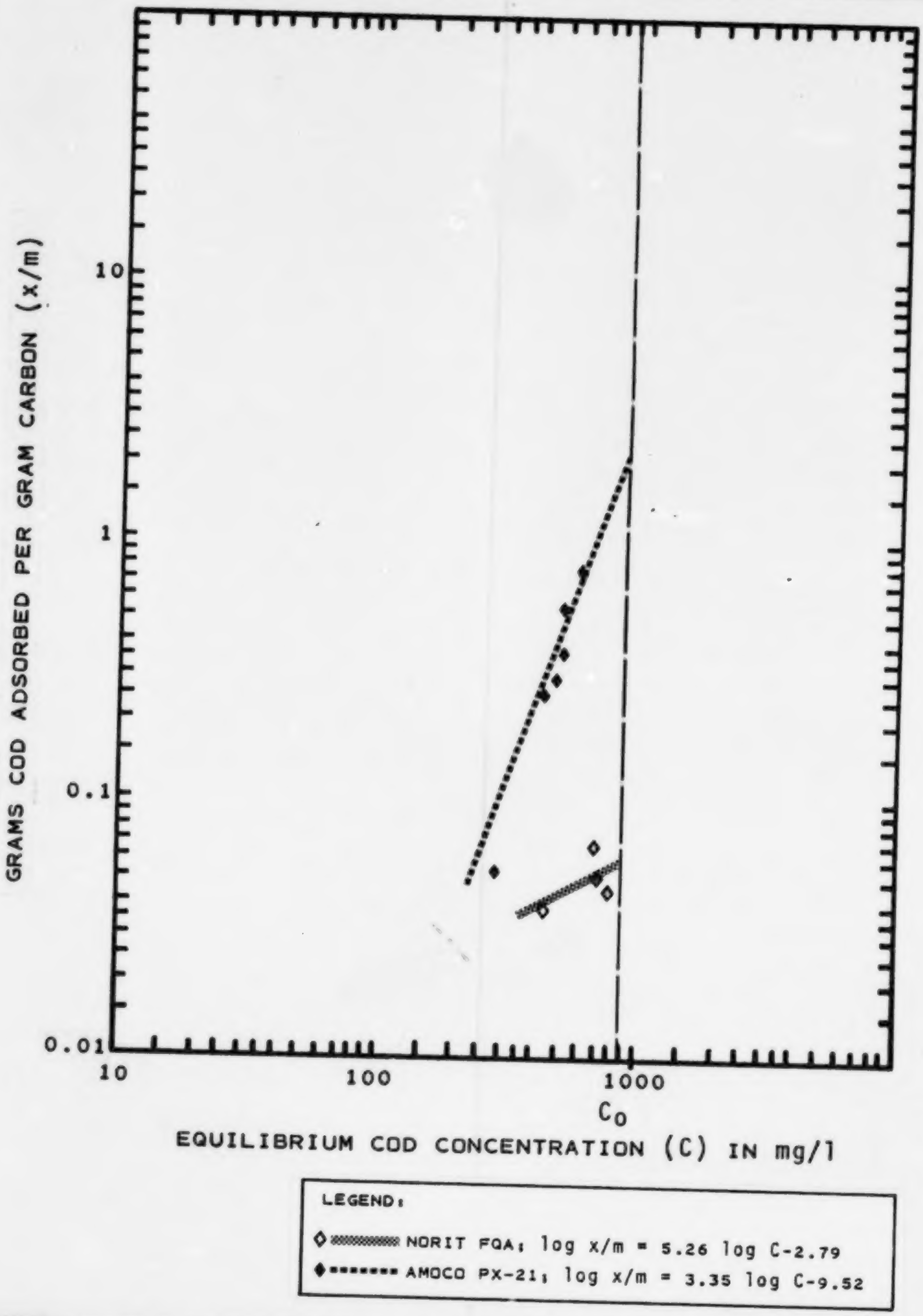

Figure 8. Freundlich adsorption isotherms for COD removal from Tannery 4 effluent (C_0=854 mg/l) using Norit FQA and Amoco PX-21 carbons.

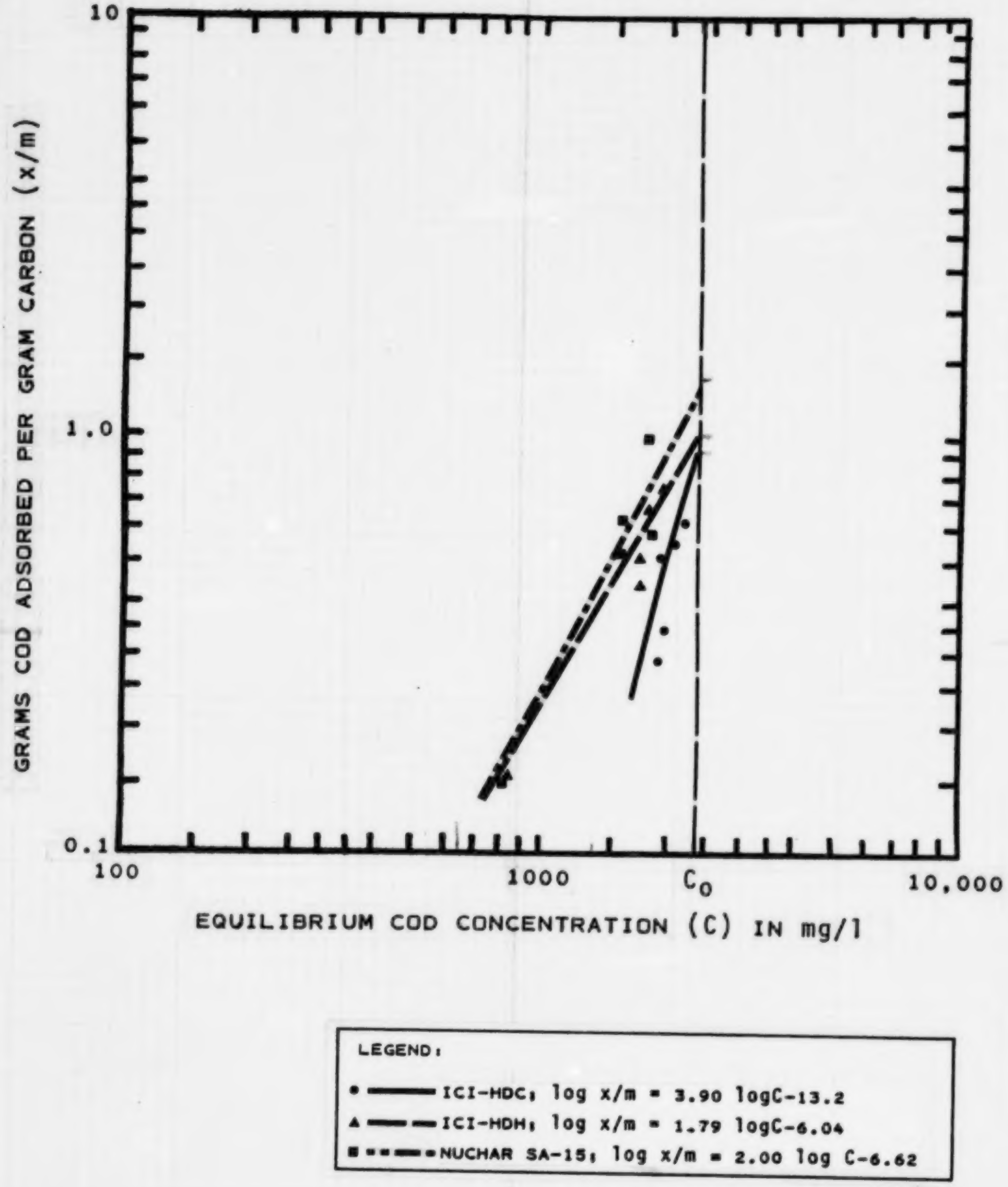

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Figure 9. Freundlich adsorption isotherms for COD removal from Tannery 1 effluent (C_0 = 2,370 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

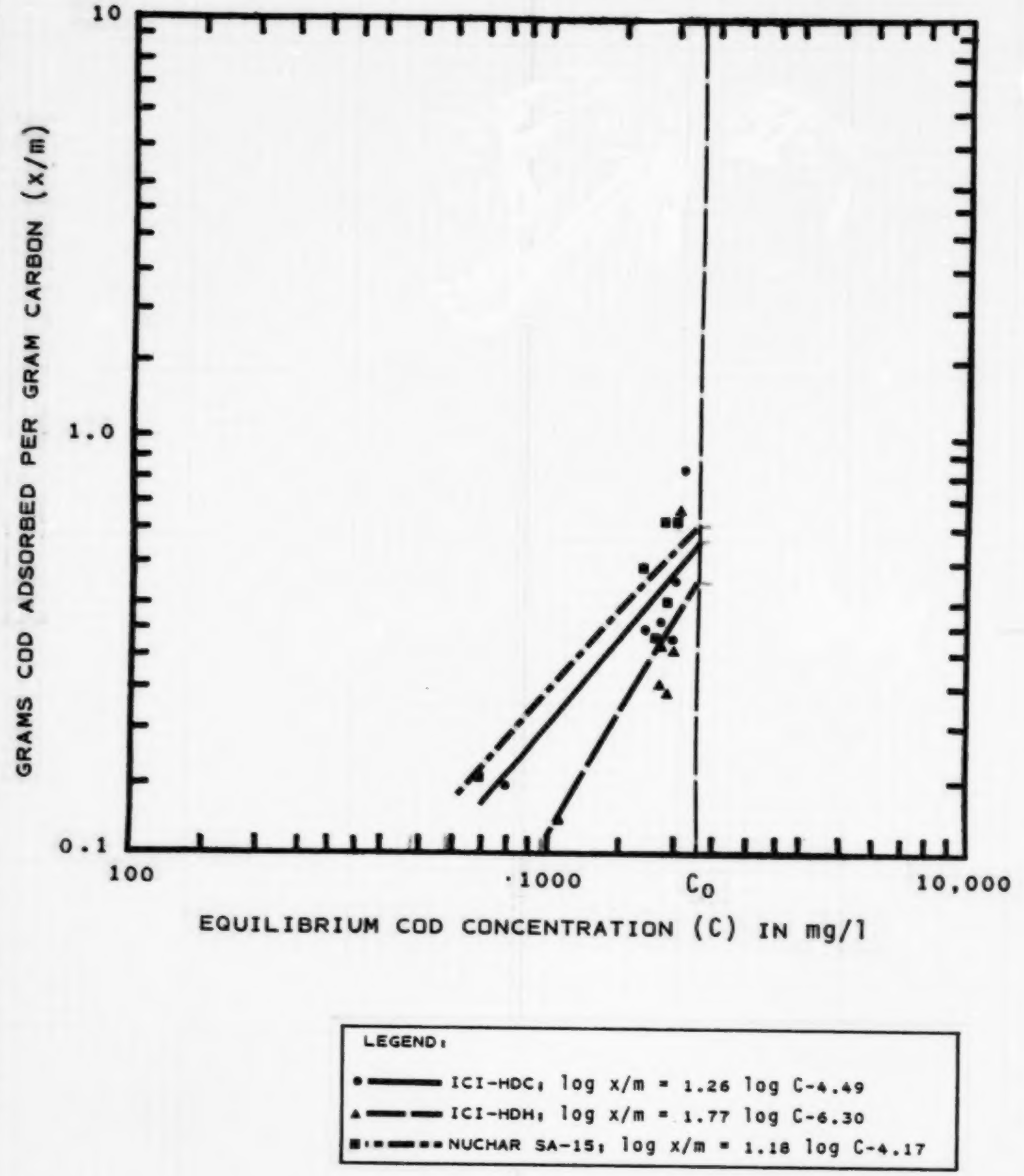

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Figure 10. Freundlich adsorption isotherms for COD removal from Tannery 9 effluent (C_0 = 2,280 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

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fivefold increase in carbon doses resulted in approximately 16 to 22 percent increases in COD removal (Table 7). Ultimate capacities of all three carbons were assumed to be equal to the observed removals at 0.3 g/l doses. These ultimate capacities were approximately 0.16 g COD/g carbon (ICI-HDC), 0.1 g COD/g carbon (ICI-HDH), and 0.35 g COD/g carbon (Nuchar SA-15).

Tannery 3

The observed COD removal efficiencies at a dose of 0.3 g/l were approximately 7 to 8 percent for ICI-HDC and ICI-HDH, but approximately twice as high for Nuchar SA-15 (Table 7). Roughly the same relationship was found to be valid at a dose of 1.5 g/l. In terms of the ultimate capacities of the three carbons for the examined effluent, Nuchar SA-15 exhibited the highest ultimate COD removal (1.2 g COD/g carbon) (Figure 11). Ultimate capacities of both ICI carbons were estimated to be approximately 0.6 g COD/g carbon.

Tannery 8

In the carbon dose range investigated, Nuchar SA-15 removed approximately twice as much COD as the two other carbons, regardless of the dose. At high doses (e.g., 1.5 g/l), COD removals were found to be 32 to 39 percent for ICI carbons, and 63 percent for Nuchar SA-15; at low doses (e.g., 0.3 g/l), the respective removals were 9 and 24 percent (Table 7). Adsorption isotherms (Figure 12) and analysis of the data presented in Table A-9 revealed that the ultimate capacity of all three carbons for COD removal from Tannery 8 effluent ranged from 0.7 to 1.4 g COD/g carbon.

Tannery 2

Effluent from this tannery was characterized by a COD content of 1,188 mg/l. Equilibration of this effluent with 0.3 g/l of ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons resulted in approximately 10 to 13 percent COD removals (Table 7). At high doses (e.g., 1.5 g/l), the two ICI carbons removed approximately 15 percent more COD than Nuchar SA-15 (42 and 32 percent, respectively). The ICI carbons were thus found to be more efficient, with ultimate capacities estimated at approximately 0.6 g COD/g carbon, while the ultimate capacity of Nuchar SA-15 was 0.45 g COD/g carbon (Figure 13).

Tannery 7

The effluent from this tannery was characterized by the highest COD content (i.e., 27,700 mg/l). Simultaneous analysis of the adsorption data (corresponding to a 1:10 dilution of the original effluent) presented in Table 7 and Figure 14 revealed that none of the three carbons tested on a tenfold dilution of the Tannery 7 waste stream was very effective in the removal of COD-contributing compounds. Regardless of the carbon doses used

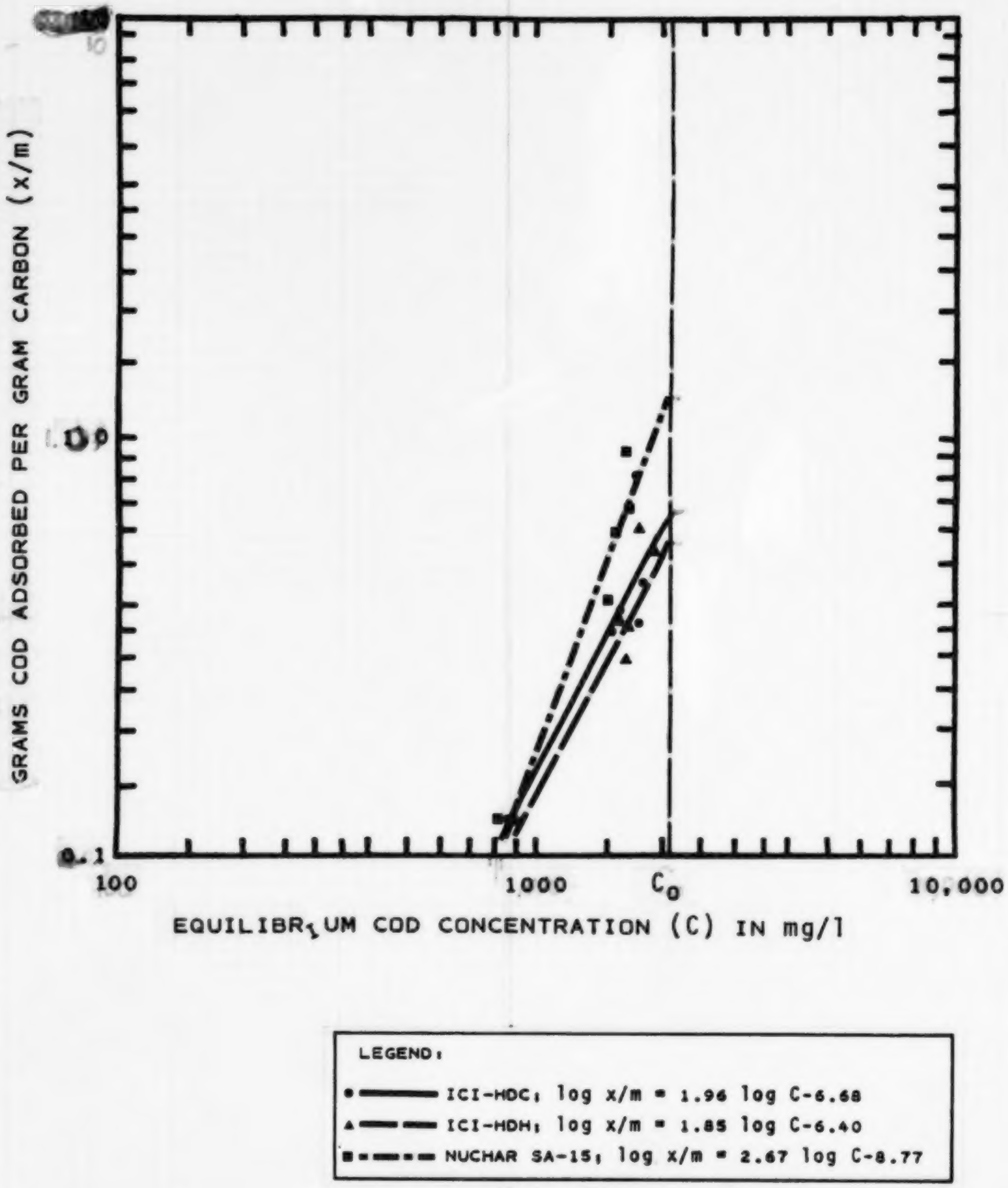

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Figure 11. Freundlich adsorption isotherms for COD removal from Tannery 3 effluent (C_o = 2,090 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

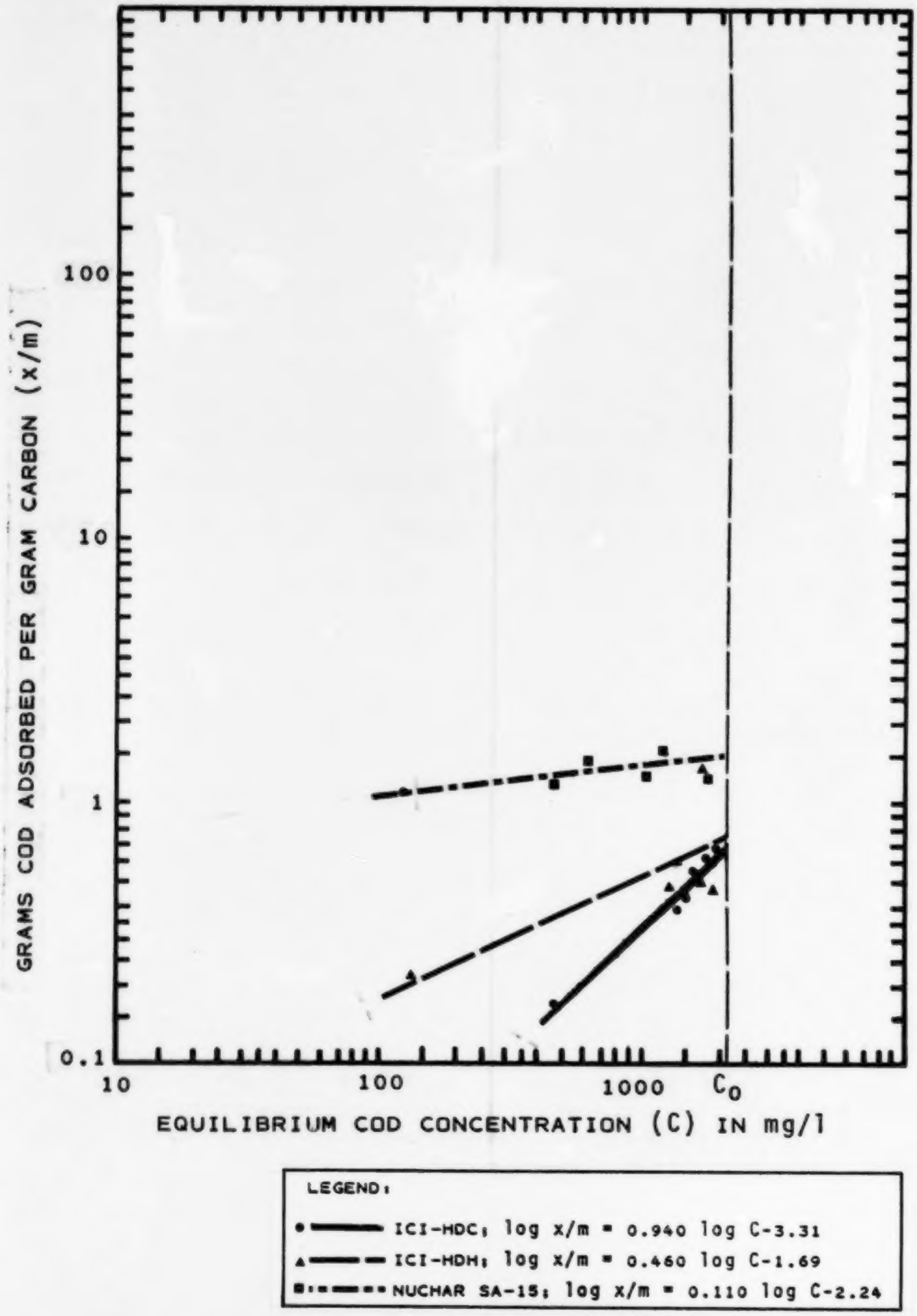

Figure 12. Freundlich adsorption isotherms for COD removal from Tannery 8 effluent (C_o = 2,160 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

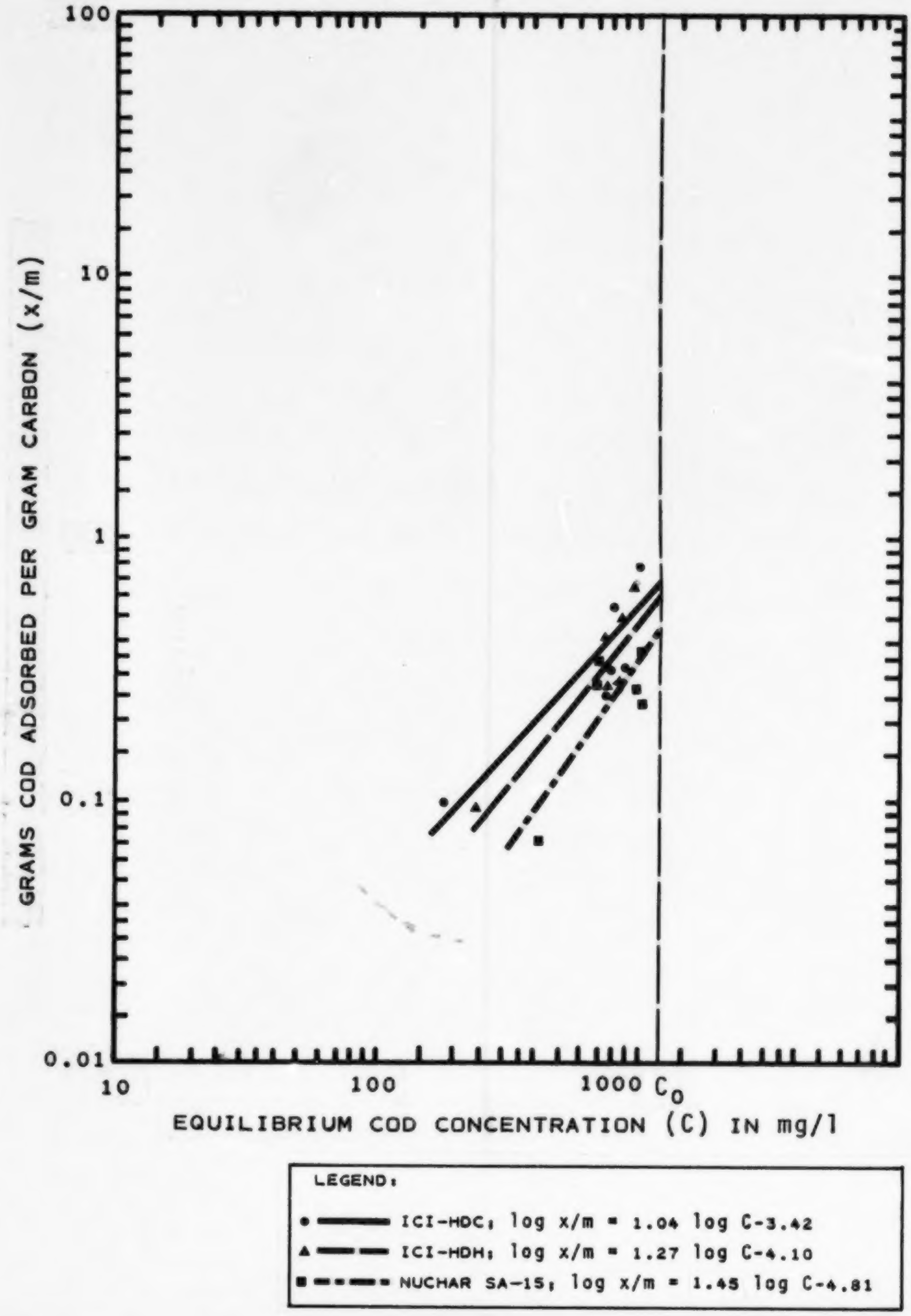

Figure 13. Freundlich adsorption isotherms for COD removal from Tannery 2 effluent (C_0 = 1,190) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

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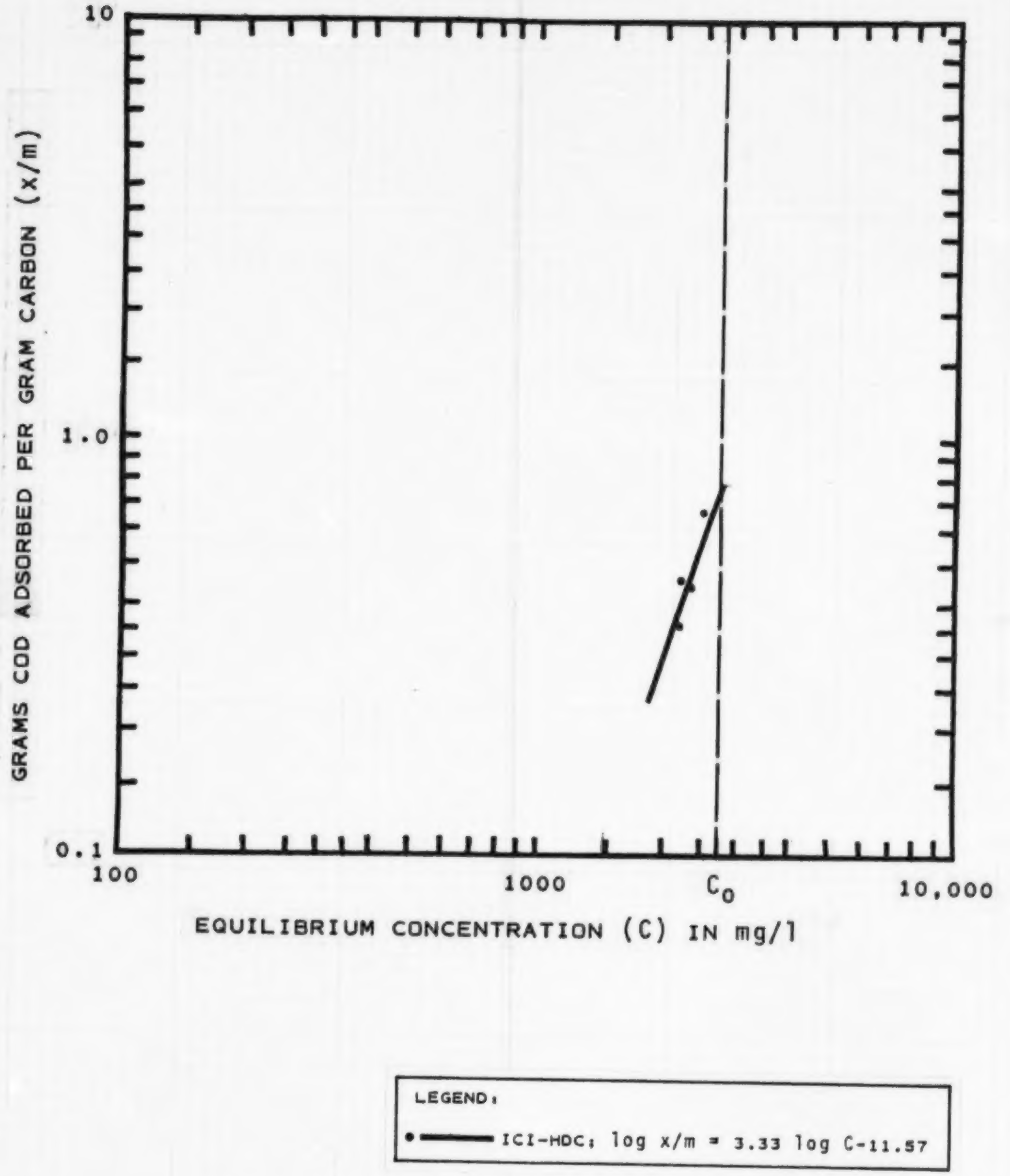

5-10

Figure 14. Freundlich adsorption isotherm for COD removal from tenfold dilution of Tannery 7 effluent (C_0 = 2,770 mg/l) using ICI-HDC carbon.

(in the range of 0.3 to 1.5 g/l), COD removals ranged from 6 to 18 percent for ICI-HDC carbon, 11 to 19 percent for ICI-HDH, and 8 to 17 for Nuchar SA-15. The corresponding ultimate capacities for all three carbons were estimated to be as follows: ICI-HDC, 0.8 g COD/g carbon (from Table A-1); ICI-HDH, 1 g COD/g carbon (from Table A-1); and Nuchar SA-15, 0.9 g COD/g carbon (Figure 14).

Tannery 5

Tannery 5 effluent was characterized by 1,200 mg/l COD. After 1 hour of equilibration of this effluent with ICI-HDH carbon, COD removals ranged from 3.4 to 14 percent corresponding to carbon doses of 0.3 and 1.5 g/l, respectively (see Table 7). At these doses, ICI-HDC carbons manifested COD removals in approximately the same range (4.5 to 18 percent, respectively), while Nuchar SA-15 manifested 7 to 21 percent, respectively. From data in Table A-12, it was concluded that the observed COD adsorption densities for the ICI carbons approached their respective ultimate capacities (i.e., 0.1 to 0.2 g COD/g carbon), while the Freundlich isotherm plots of Nuchar SA-15 indicated an ultimate capacity of 0.35 g COD/g carbon (Figure 15).

THA

Tannery 0

Among the six carbons tested for the removal of THA from Tannery 0 effluents (27.3 mg/l), at carbon doses of 0.3 g/l, the best results were obtained with Nuchar SA-15 (49.5 percent), Amoco PX-21 (43 percent), ICI-HDC (38.5 percent), and ICI-HDH (30 percent) (Table 8). Norit FQA and Westates WO-841 resulted in only 22 and 10 percent THA removal, respectively. At 0.6 g/l doses, the observed THA removals were 66, 67, 52, 45, 38, and 16 percent, respectively. Freundlich adsorption isotherm plots of the experimental data (Figures 16 and 17) indicated that ultimate THA removal capacities for Amoco PX-21, Nuchar SA-15, and ICI-HDC were approximately 0.08 g THA/g carbon, while those for ICI-HDH, Norit FQA, and Westates WO-841 were 0.04, 0.01, and 0.02 g THA/g carbon, respectively.

Tannery 4

Effluent from this tannery contained approximately 49.6 mg/l THA; equilibration with an excess of both Amoco PX-21 and Nuchar SA-15 carbons, in doses of 0.3 to 1.5 g/l, resulted in THA removals ranging from 9 to 48 percent, and 3 to 15 percent, respectively (Table 8). The other carbons were found to be either completely ineffective (Norit FQA, Westates WO-841), or less effective than the above two carbons (resulting in up to 9 percent THA removal in the same dose range). These data indicated ultimate capacities of ICI carbons and Nuchar SA-15 to be approximately 0.003 to 0.006 g THA/g carbon (Figure 18 and Table A-3); the ultimate capacity of Amoco PX-21 was found to be 0.01 g THA/g carbon (Figure 19).

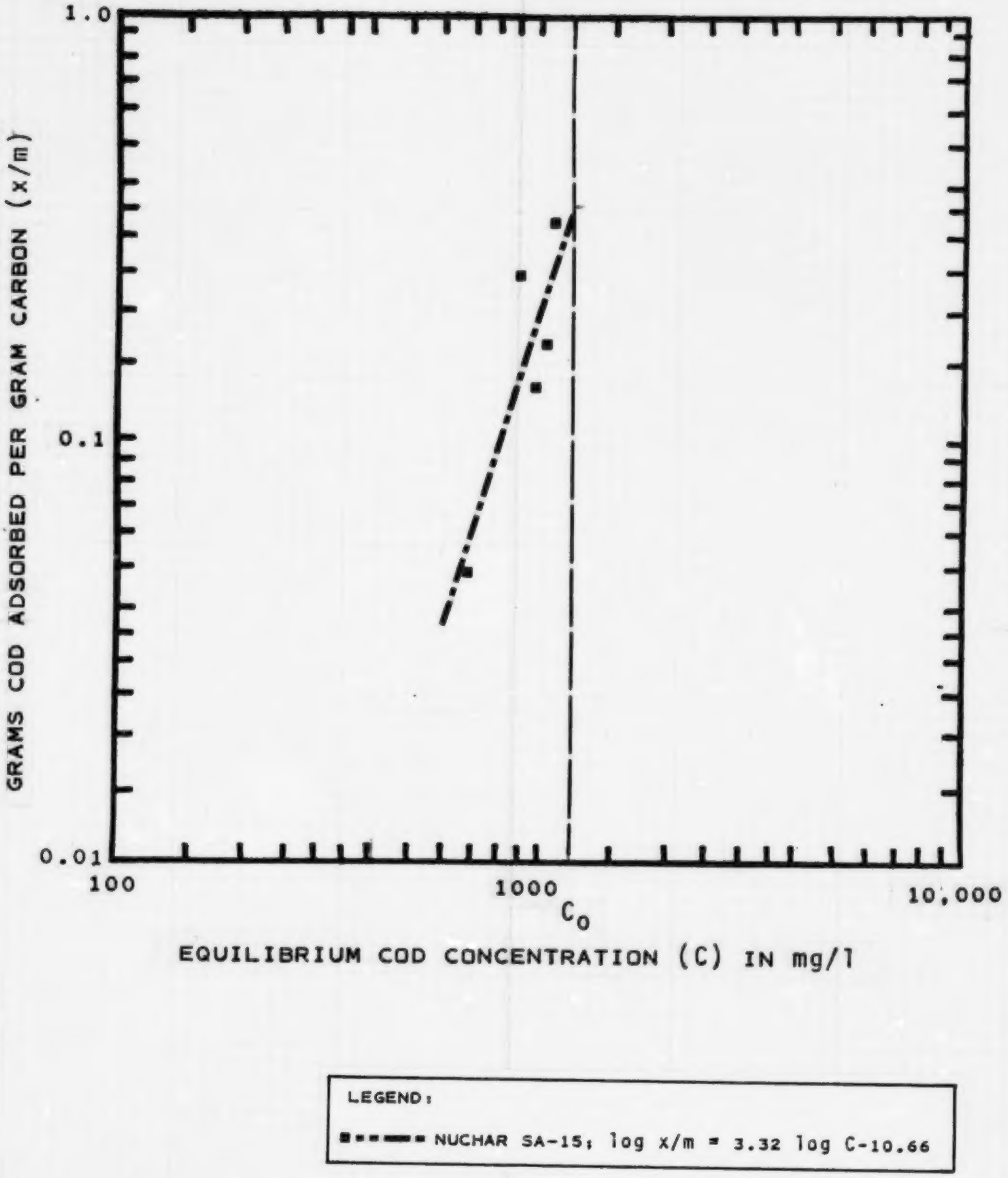

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Figure 15. Freundlich adsorption isotherm for COD removal from Tannery 5 effluent (C_0 = 1,190 mg/l) using Nuchar SA-15 carbon.

TABLE 8. PERCENT THA REMOVAL AS A FUNCTION OF CARBON DOSE*

Tannery	Initial Concentration (mg/l)	Carbon Dose (g/l)																	
		0.3						0.6						1.5					
		HDC	HDH	NUCH	NOR	WEST	AMO	HDC	HDH	NUCH	NOR	WEST	AMO	HDC	HDH	NUCH	NOR	WEST	AMO
0	27.3	38.5	30.0	49.5	21.6	9.9	42.9	52.0	44.7	66.3	38.1	16.1	66.7	68.1	64.1	83.2	66.7	26.7	86.4
1	179	2.5	4.7	4.6	-	-	-	5.0	8.5	8.4	-	-	-	12.2	16.6	16.6	-	-	-
2	63.8	21.3	15.7	15.2	-	-	-	36.5	27.3	26.6	-	-	-	62.9	48.9	48.3	-	-	-
3	120	62.5	67.8	35.0	-	-	-	72.7	74.1	45.5	-	-	-	82.7	80.7	58.4	-	-	-
4	49.6	1.8	1.8	3.4	0	0	9.3	3.6	3.8	6.6	0	0	11.3	8.9	9.1	14.7	0	0	47.6
5	55	1.8	1.8	2.9	-	-	-	3.6	3.6	5.8	-	-	-	8.9	8.9	14.0	-	-	-
6	212	5.3	4.0	3.7	-	-	-	9.8	7.5	7.4	-	-	-	20.5	15.5	17.5	-	-	-
7	325†	11.6	13.4	17.2	-	-	-	18.6	20.3	23.5	-	-	-	30.3	31.0	32.4	-	-	-
8	26.5	10.9	13.6	8.7	-	-	-	20.4	25.3	16.6	-	-	-	43.8	50.2	36.6	-	-	-
9	225	6.0	5.0	5.5	-	-	-	11.6	9.5	10.7	-	-	-	26.1	20.2	24.5	-	-	-

* HDC = ICI-HDC
HDH = ICI-HDH
NUCH = Nuchar SA-15
NOR = Norit FQA
WEST = Westates WO-841
AMO = Amoco PX-21.

† Corresponds to 1:10 dilution of the original effluent.

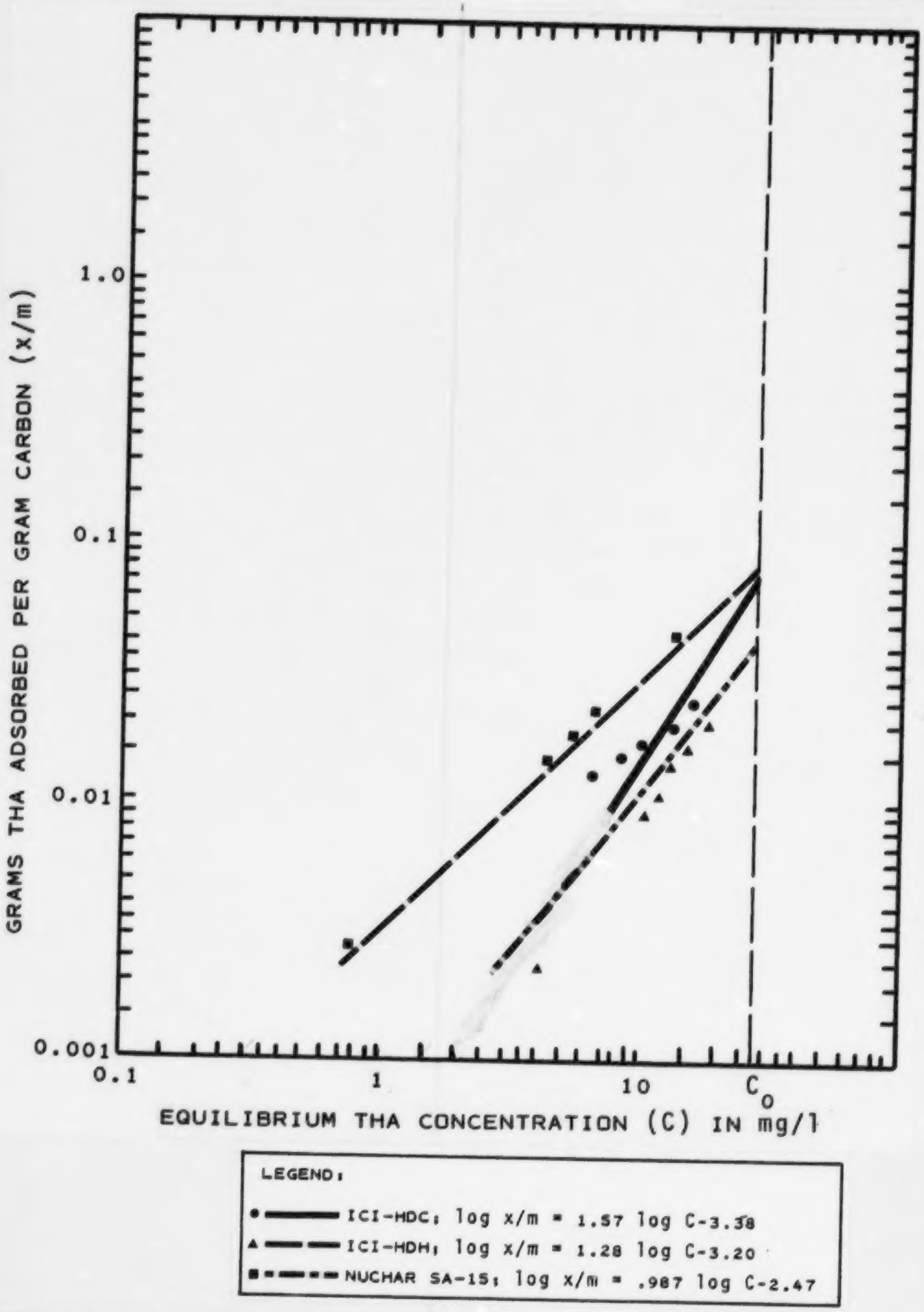

Figure 16. Freundlich adsorption isotherms for THA removal from Tannery O effluent (C_0 = 27.3 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

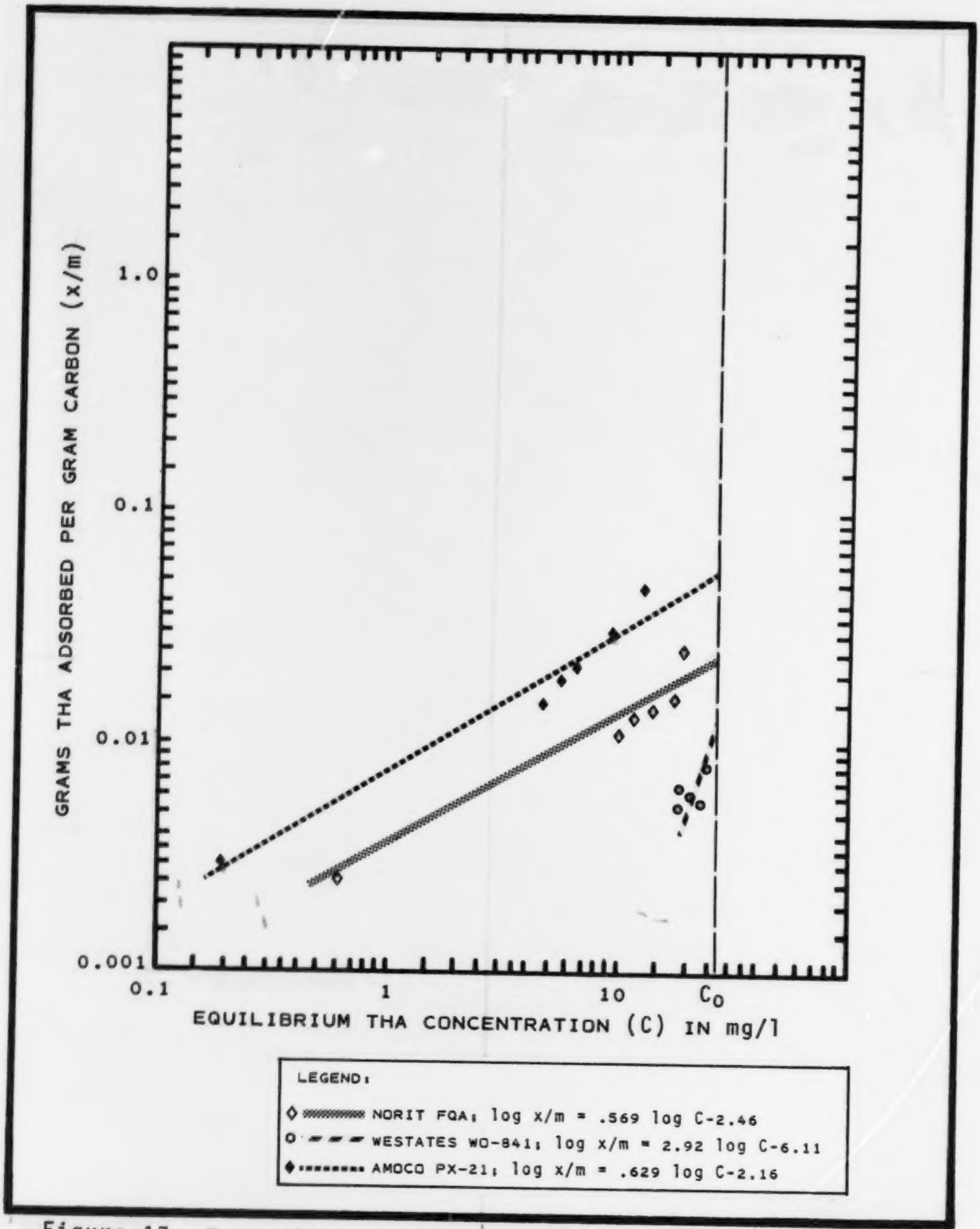

Figure 17. Freundlich adsorption isotherms for THA removal from Tannery O effluent (C_0 = 27.3 mg/l) using Norit FQA, Westates WO-841, and Amoco PX-21 carbons.

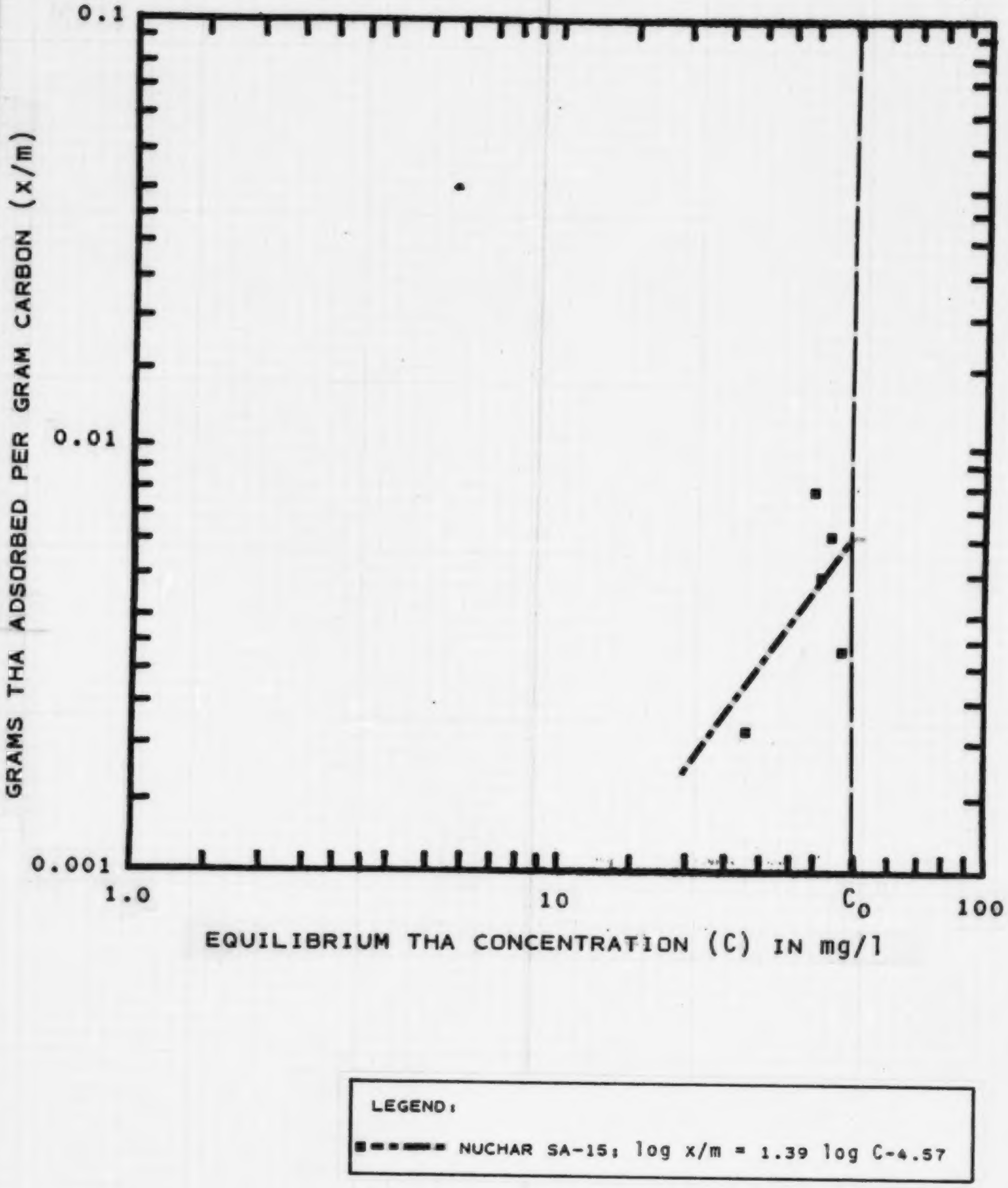

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Figure 18. Freundlich adsorption isotherm for THA removal from Tannery 4 effluent (C_0 = 49.6 mg/l) using Nuchar SA-15 carbon.

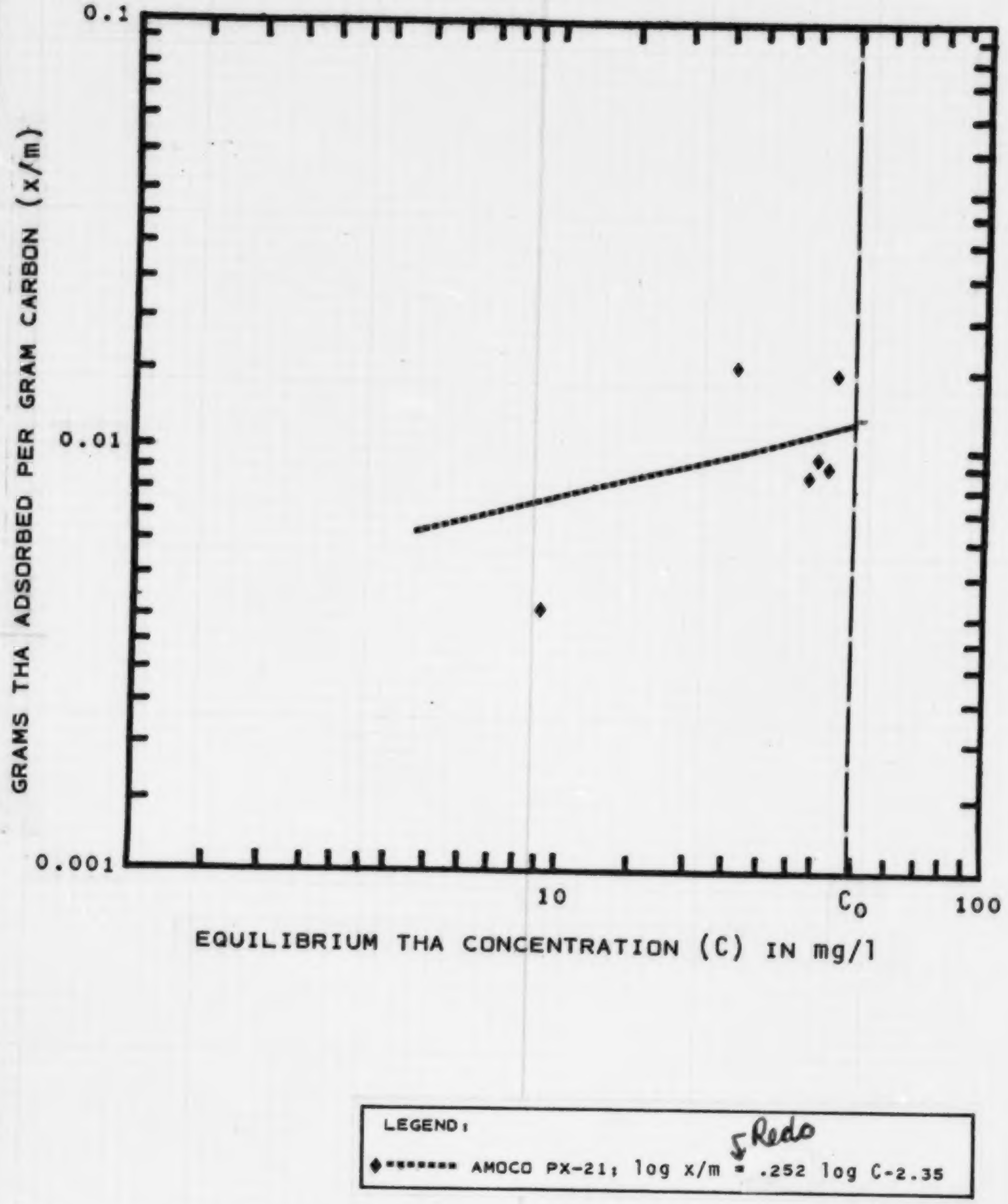

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Figure 19. Freundlich adsorption isotherm for THA removal from Tannery 4 effluent (C_0 = 49.6 mg/l) using Amoco PX-21 carbon.

Tannery 1

The three carbons tested for the removal of THA compounds from Tannery 1 effluent yielded approximately the same results: 2.5 to 5 percent removals at doses of 0.3 g/l, and 12 to 17 percent removals at doses of 1.5 g/l (Table 8). The corresponding ultimate capacities were estimated to be 0.02 to 0.06 g THA/g carbon.

Tannery 9

Tannery 9 effluent was found to contain 255 mg/l THA compounds. Equilibration of this compound with 0.3 g/l of each carbon (i.e., Nuchar SA-15, ICI-HDC, and ICI-HDH) resulted in approximately 5.5, 6, and 5 percent THA removals, respectively (Table 8). These low removal efficiencies indicated close proximity to the saturation of the adsorbent; isotherm plots of the adsorption data (Figure 20) showed that the observed THA removals at low carbon doses were essentially the ultimate capacities of each respective carbon for THA removal from this particular effluent. Numerical values of the ultimate capacities for all three carbons were estimated to be approximately 0.05 g THA/g carbon. These ultimate capacities indicated that even at doses of 1.5 g/l, the expected THA removals would be in the range of 20 to 30 percent (see Table 8).

Tannery 6

Adsorption data for the removal of THA compounds from Tannery 6 effluents are presented in Table 8 and Figure 21. Low removal efficiencies for all three carbons at doses of 0.3 and 0.6 g/l (4 to 5 percent, and 7 to 10 percent, respectively) indicated a close proximity to their surface saturations. As shown in Table 8, at doses of 1.5 g/l, THA removals were in the range of 15 to 20 percent. Ultimate capacities of all three carbons for this particular effluent were estimated to be in the range of 0.03 to 0.04 g THA/g carbon (Figure 21).

Tannery 3

Regardless of the carbon doses used, all three carbons were found to be very effective in the removal of THA compounds from Tannery 3 effluents (Table 8). Within the carbon range of 0.3 to 1.5 g/l, the best removals were accomplished using ICI carbons (63 to 83 percent), followed by Nuchar SA-15 (35 to 58 percent). Freundlich isotherm plots (Figure 22) and analysis of the data presented in Table A-8 indicated that the ultimate capacities of all three carbons were approximately 0.3 to 0.4 g THA/g carbon.

Tannery 8

At the lowest examined carbon doses (0.3 g/l), the observed THA removals were in the range of 9 to 14 percent for all three

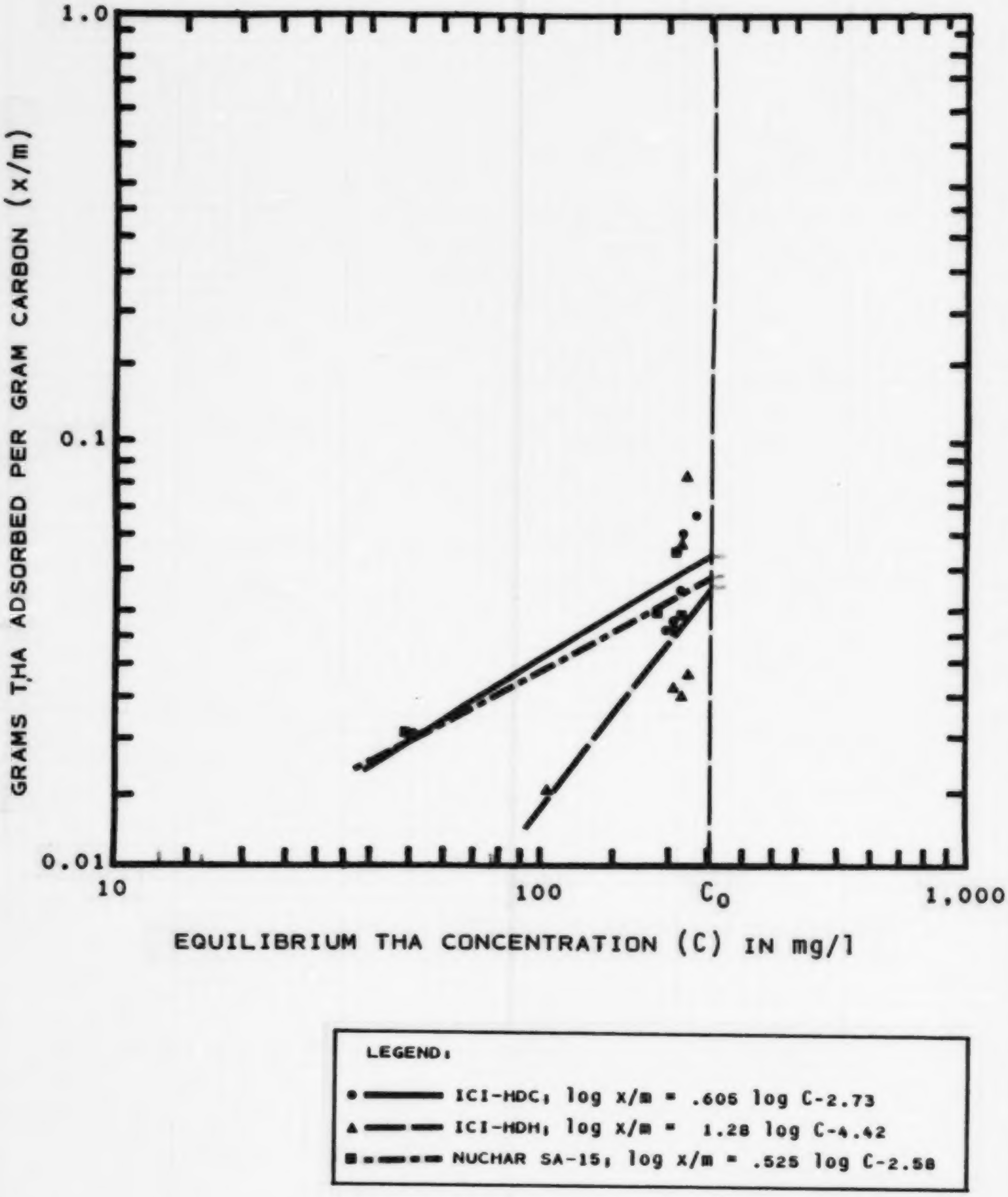

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Figure 20. Freundlich adsorption isotherms for THA removal from Tannery 9 effluent (C_o = 255 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

133 16

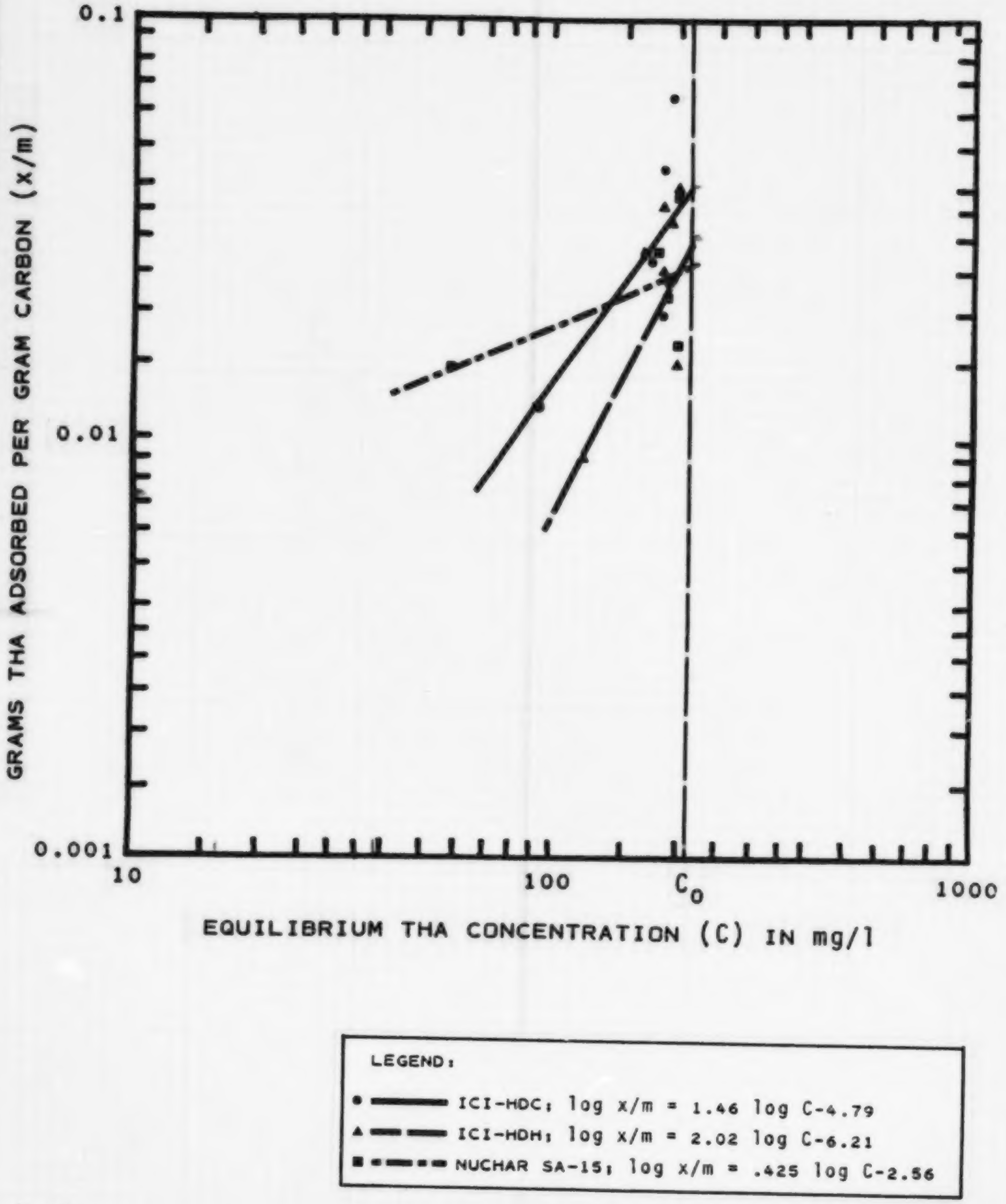

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Figure 21. Freundlich adsorption isotherms for THA removal from Tannery 6 effluent (C_o = 212 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

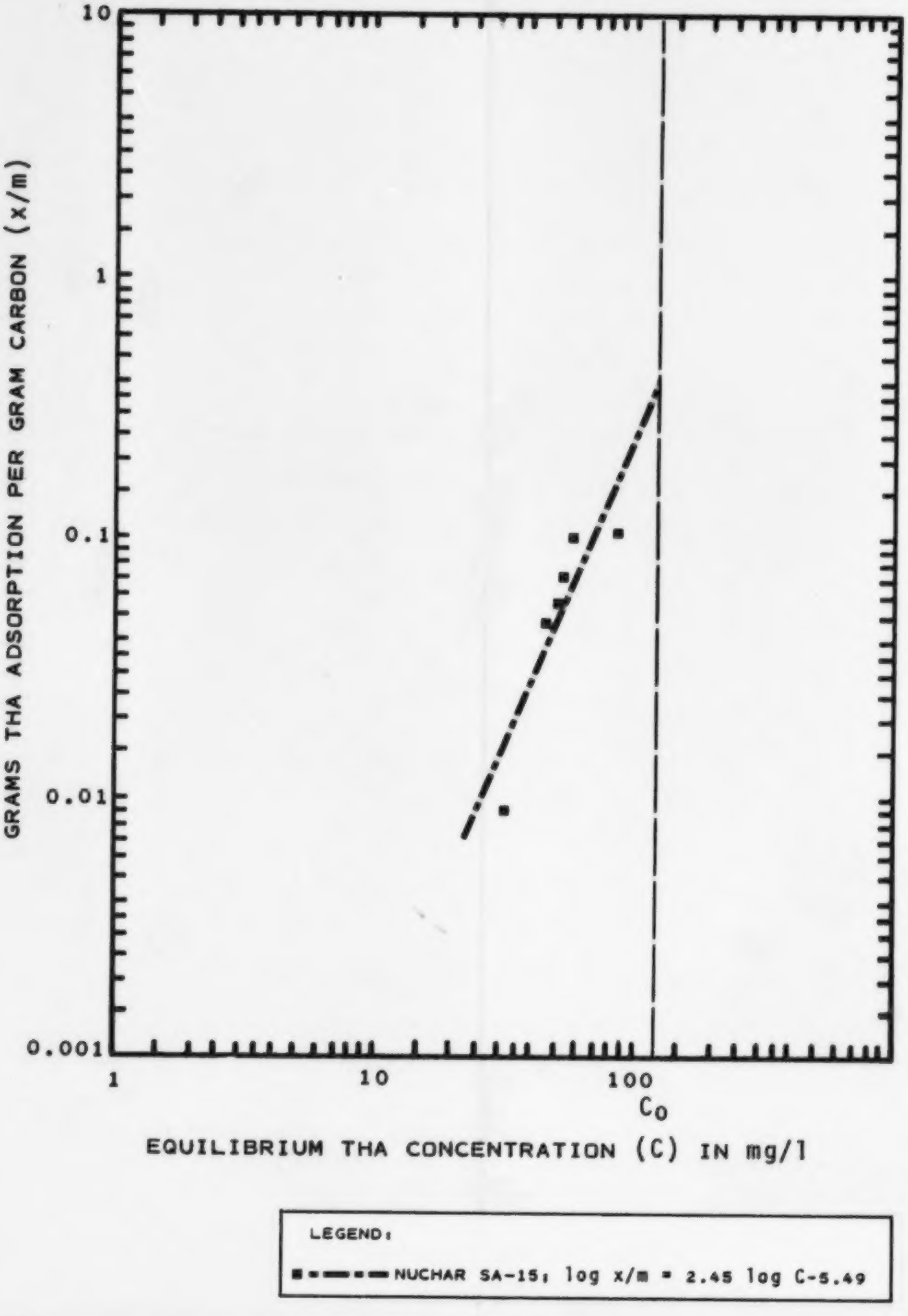

Figure 22. Freundlich adsorption isotherms for THA removal from Tannery 3 effluent (C_0 = 120 mg/l) using Nuchar SA-15 carbon.

carbons; at doses of 0.6 g/l, there was an 8 to 11 percent increase in removal efficiency (Table 8). At an excess of the available surface areas (e.g., 1.5 g/l), all three carbons exhibited an additional twofold increase in THA removals. Extrapolation to the initial effluent THA concentration (26.5 mg/l) indicated saturation capacities of all three carbons to be approximately 0.01 g THA/g carbon (Figure 23).

Tannery 2

Tannery 2 effluent was found to contain 63.8 mg/l THA. Equilibration of this effluent with 0.3 g/l of each carbon resulted in approximately 15 percent removal with Nuchar SA-15, 16 percent with ICI-HDH, and 21 percent with ICI-HDC (Table 8). At high carbon doses (1.5 g/l), the respective THA removals were 48, 49, and 63 percent (Table 8). Isotherm plots of these data showed ultimate capacities of all three carbons to be 0.04 to 0.05 g THA/g carbon (Figure 24).

Tannery 7

Of all the tanneries sampled, Tannery 7 effluent was found to contain the highest concentration of THA compounds (3,250 mg/l). Treatment of a 1:10 dilution of this effluent with 0.3 to 1.5 g/l of each of the three carbons resulted in approximately the same removals of these compounds, ranging from 12 to 17 percent, and 30 to 32 percent, respectively. The resulting capacities of all three carbons for the removal of THA compounds from a tenfold dilution of Tannery 7 effluent were estimated to be 0.2 to 0.5 g THA/g carbon (Figure 25).

Tannery 5

Analysis of Tannery 5 effluent indicated the presence of 55 mg/l THA compounds (Table 8). Treatment of this effluent with 0.3 g/l Nuchar SA-15, ICI-HDH, and ICI-HDC resulted in very low THA removals (2 to 3 percent); even a fivefold increase in the available carbon surface area did not result in an appreciable increase in THA removals. From Figure 26 and Table A-12, the ultimate capacities of all three carbons were estimated to be approximately 0.003 to 0.005 g THA/g carbon.

BOD

Tannery 0

Tannery 0 effluent analyses showed the presence of 228 mg/l BOD-contributing compounds, the lowest among all 10 tannery effluent samples. Tests with this effluent revealed that, of the six carbons tested, three carbons (ICI-HDC, ICI-HDH, and Amoco PX-21), when applied at a high dose of 1.5 g/l, removed 70, 62, and 62 percent BOD, respectively (Table 9). The next best carbons appeared to be Nuchar SA-15 and Norit FQA, accomplishing

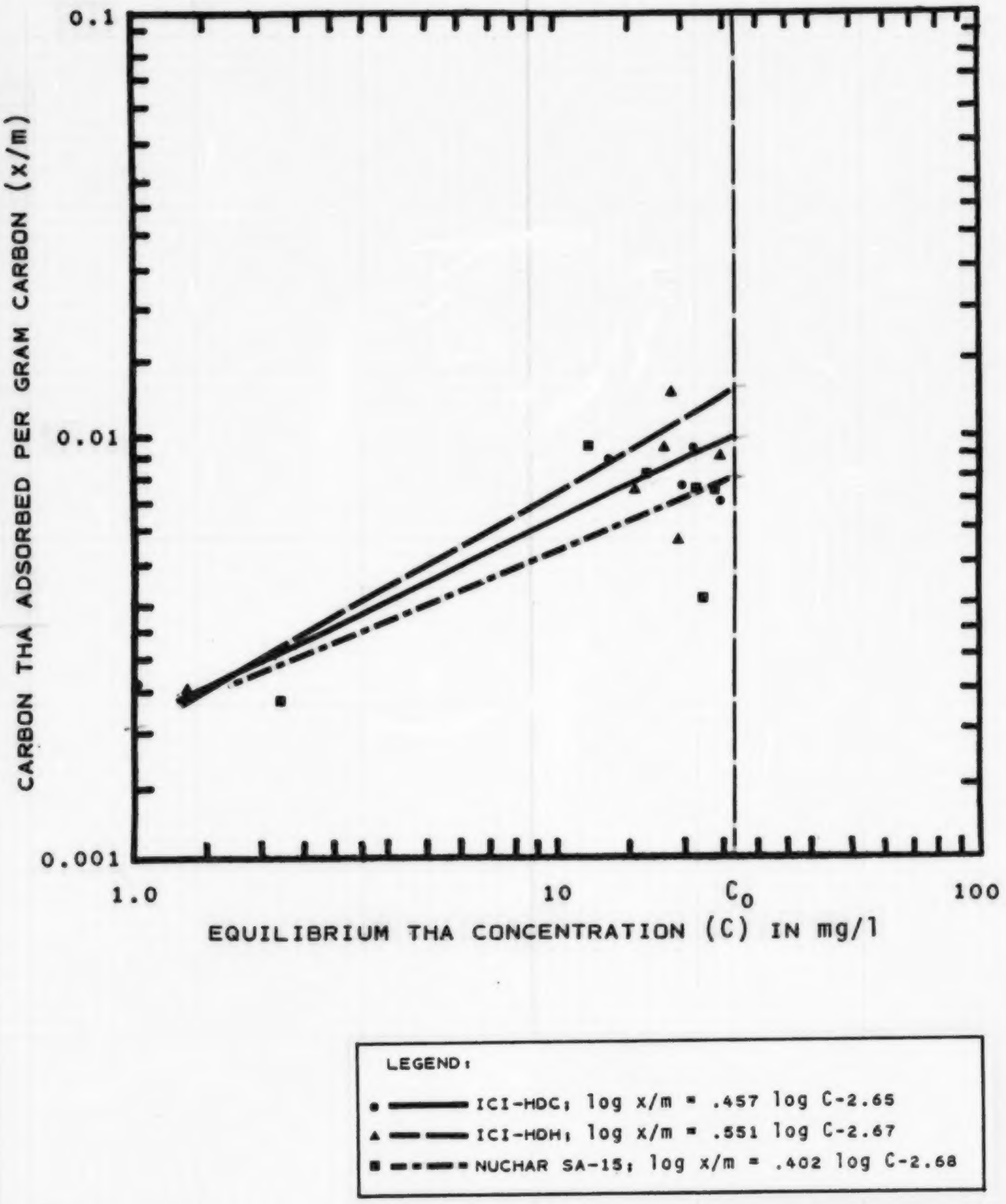

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Figure 23. Freundlich adsorption isotherms for THA removal from Tannery 8 effluent (C_0 = 26.5 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

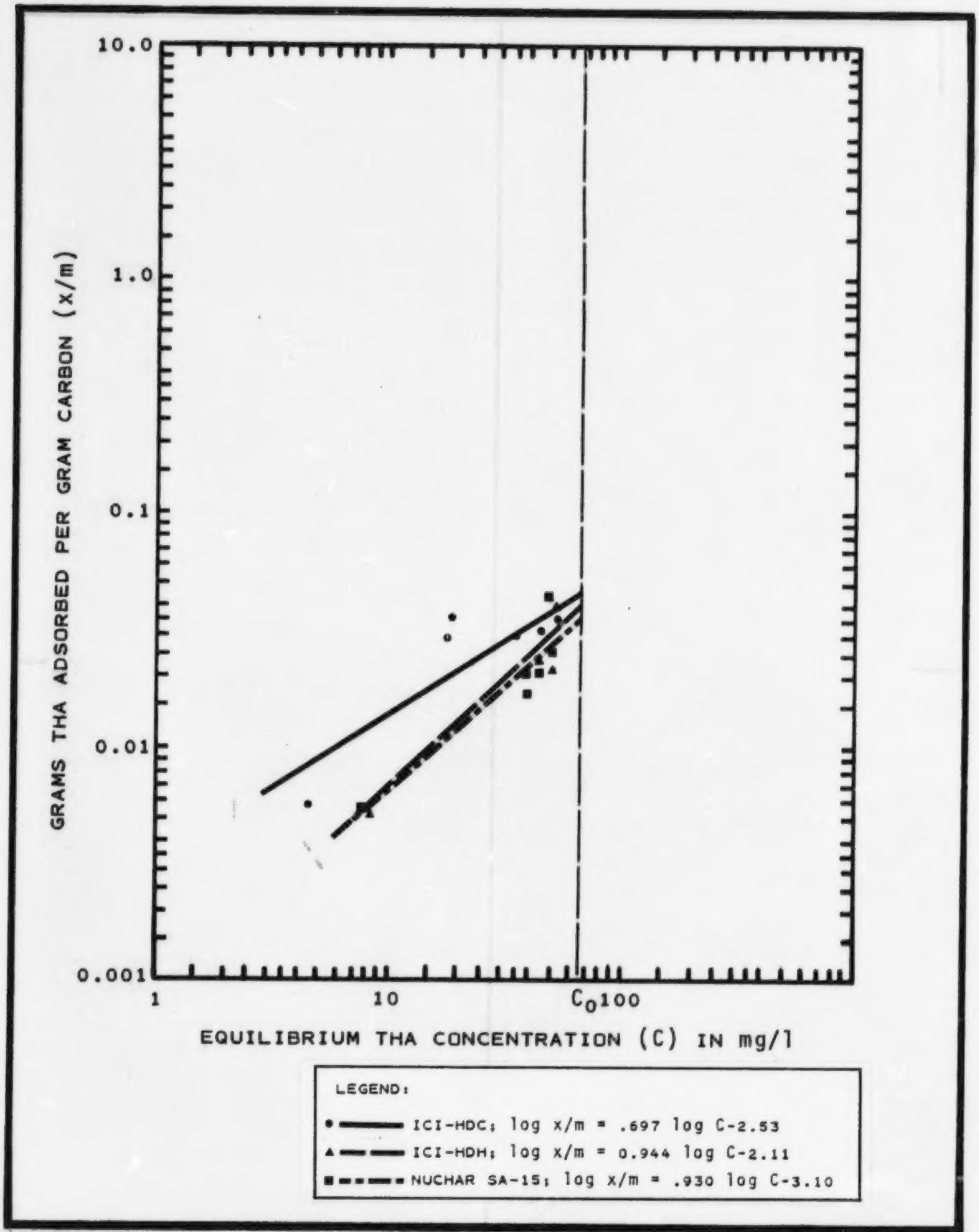

Figure 24. Freundlich adsorption isotherms for THA removal from Tannery 2 effluent (C_0 = 63.8 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

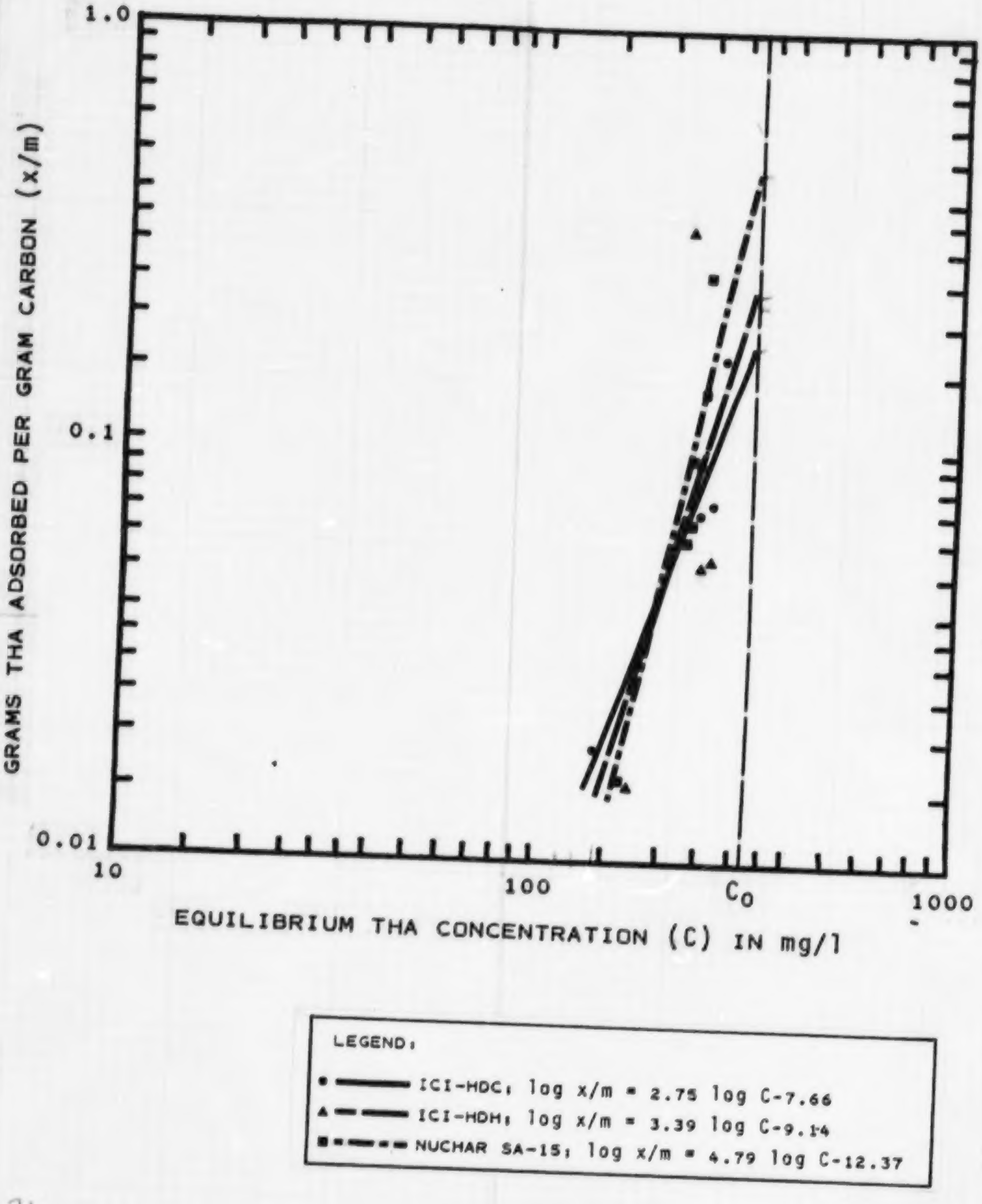

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Figure 25. Freundlich adsorption isotherms for THA removal from tenfold dilution of Tannery 7 effluent (C_0 = 325 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

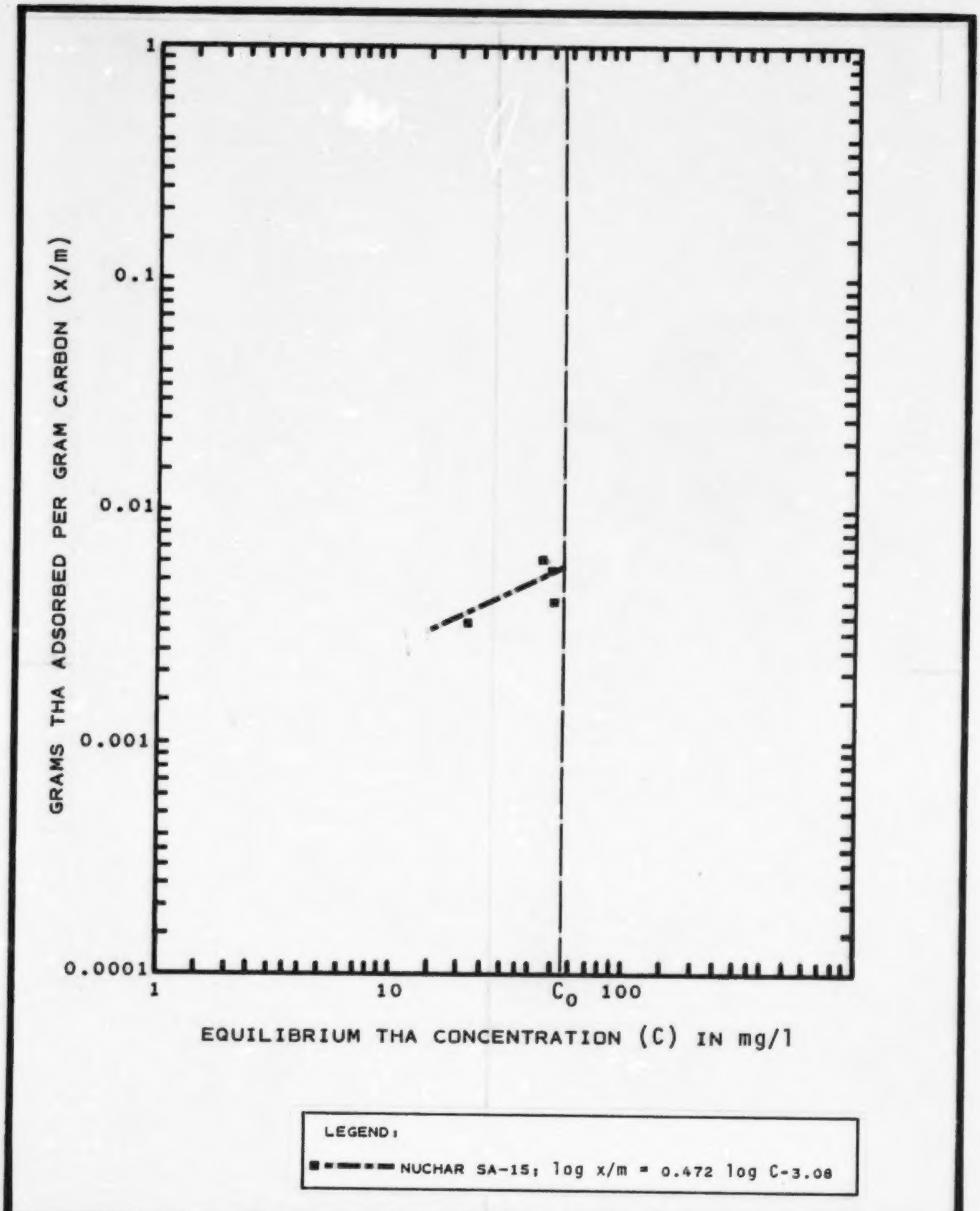

Figure 26. Freundlich adsorption isotherm for THA removal from Tannery 5 effluent (C_0 = 55 mg/l) using Nuchar SA-15 carbon.

TABLE 9. PERCENT BOD REMOVAL AS A FUNCTION OF CARBON DOSE*

Tannery	Initial Concentration (mg/l)	Carbon Dose (g/l)																	
		0.3						0.6						1.5					
		HDC	HDH	NUCH	NOR	WEST	AMO	HDC	HDH	NUCH	NOR	WEST	AMO	HDC	HDH	NUCH	NOR	WEST	AMO
0	228	48.4	42.8	30.4	29.8	9.5	38.5	58.4	51.5	39.0	37.3	15.3	48.4	69.7	61.9	50.0	46.9	25.4	61.6
1	1,381	20.2	14.6	21.5	-	-	-	28.4	21.8	28.5	-	-	-	39.8	32.9	37.8	-	-	-
2	738	1.6	1.3	12.1	-	-	-	3.2	2.6	20.4	-	-	-	7.9	6.6	35.6	-	-	-
3	988	2.7	1.1	4.0	-	-	-	4.9	2.1	6.9	-	-	-	10.4	5.0	12.9	-	-	-
4	574	2.6	0	2.2	6.6	0	18.9	5.2	0	4.2	11.6	0	25.2	12.9	0	9.5	21.6	0	33.7
5	590	10.4	3.3	26.7	-	-	-	16.9	6.4	36.4	-	-	-	28.3	14.5	49.4	-	-	-
6	1,920	0	2.8	26.7	-	-	-	0	5.2	41.6	-	-	-	0	10.6	63.1	-	-	-
7	1,620†	11.1	10.6	17.7	-	-	-	16.9	17.0	26.3	-	-	-	26.3	27.9	39.0	-	-	-
8	1,050	8.2	2.9	20.9	-	-	-	15.5	5.8	35.0	-	-	-	33.2	15.3	58.3	-	-	-
9	1,295	6.9	5.8	8.0	-	-	-	12.6	10.3	14.2	-	-	-	24.8	19.7	27.1	-	-	-

* HDC = ICI-HDC
HDH = ICI-HDH
NUCH = Nuchar SA-15
NOR = Norit FQA
WEST = Westates WO-841
AMO = Amoco PX-21.

† Corresponds to 1:10 dilution of the original sample.

approximately 50 and 47 percent BOD removals, respectively, followed by Westates WO-841 (25 percent) (Table 9). Removals at low doses (0.3 g/l) were 39, 30, 48, 30, 43, and 10 percent for Amoco PX-21, Nuchar SA-15, ICI-HDC, Norit FQA, ICI-HDH, and Westates WO-841, respectively. Ultimate capacities of these carbons (estimated from data in Figure 27 and Table A-1) were found to be in the following descending order: Amoco PX, ICI-HDC, ICI-HDH, Norit FQA, Nuchar SA-15, and Westates WO-841, ranging from approximately 0.35 to 2.8 g BOD/g carbon.

Tannery 4

In the presence of a carbon concentration of 1.5 g/l, BOD removals were found to be 0, 0, 9.5, 13, 22, and 34 percent for ICI-HDH, Westates WO-841, Nuchar SA-15, ICI-HDC, Norit FQA, and Amoco PX-21, respectively (Table 9). At a low dose (0.3 g/l), the respective removals were 0, 0, 2, 3, 7, and 19 percent (Table 9). The ultimate capacities of the carbons were estimated from the data (Figures 28 and 29, and Tables A-3 and A-4) to be highest for Amoco PX-21 and Norit FQA (approximately 1 and 0.2 g BOD/g carbon, respectively), followed by ICI-HDC and Nuchar SA-15 (approximately 0.05 and 0.04 g BOD/g carbon, respectively). Both ICI-HDH and Westates WO-841 appeared to be the least efficient; their ultimate capacities were estimated to be below 0.02 g BOD/g carbon (from Tables A-3 and A-4).

Tannery 1

Evaluation of the results presented in Table 9 showed that, at a dose of 1.5 g/l, the observed BOD removals from Tannery 1 effluents were 38, 33, and 40 percent for Nuchar SA-15, ICI-HDH, and ICI-HDC, respectively. At a lower dose (0.6 g/l), the respective removals were 29, 22, and 28 percent, while at the lowest dose studied (0.3 g/l), they ranged from 15 to 22 percent. The ultimate capacities of all three carbons ranged from approximately 0.75 to 1 g BOD/g carbon (estimated from Table A-5 data).

Tannery 9

Tannery 9 effluent was found to contain 1,300 mg/l BOD-contributing compounds. At a dose of 0.3 g/l, all three carbons adsorbed approximately 6 to 8 percent BOD; increasing the carbon doses from 0.3 to 0.6 g/l resulted in a 4 to 6 percent increase in BOD removal (Table 9). At carbon doses of 1.5 g/l, the observed BOD removals were increased to 20 to 27 percent. In view of the BOD content of this effluent, the ultimate capacities of these carbons were estimated to be in the range of 0.3 to 0.4 g BOD/g carbon (Figure 30). Thus, the observed removals at 0.3 g/l doses of all three carbons approached their respective ultimate values.

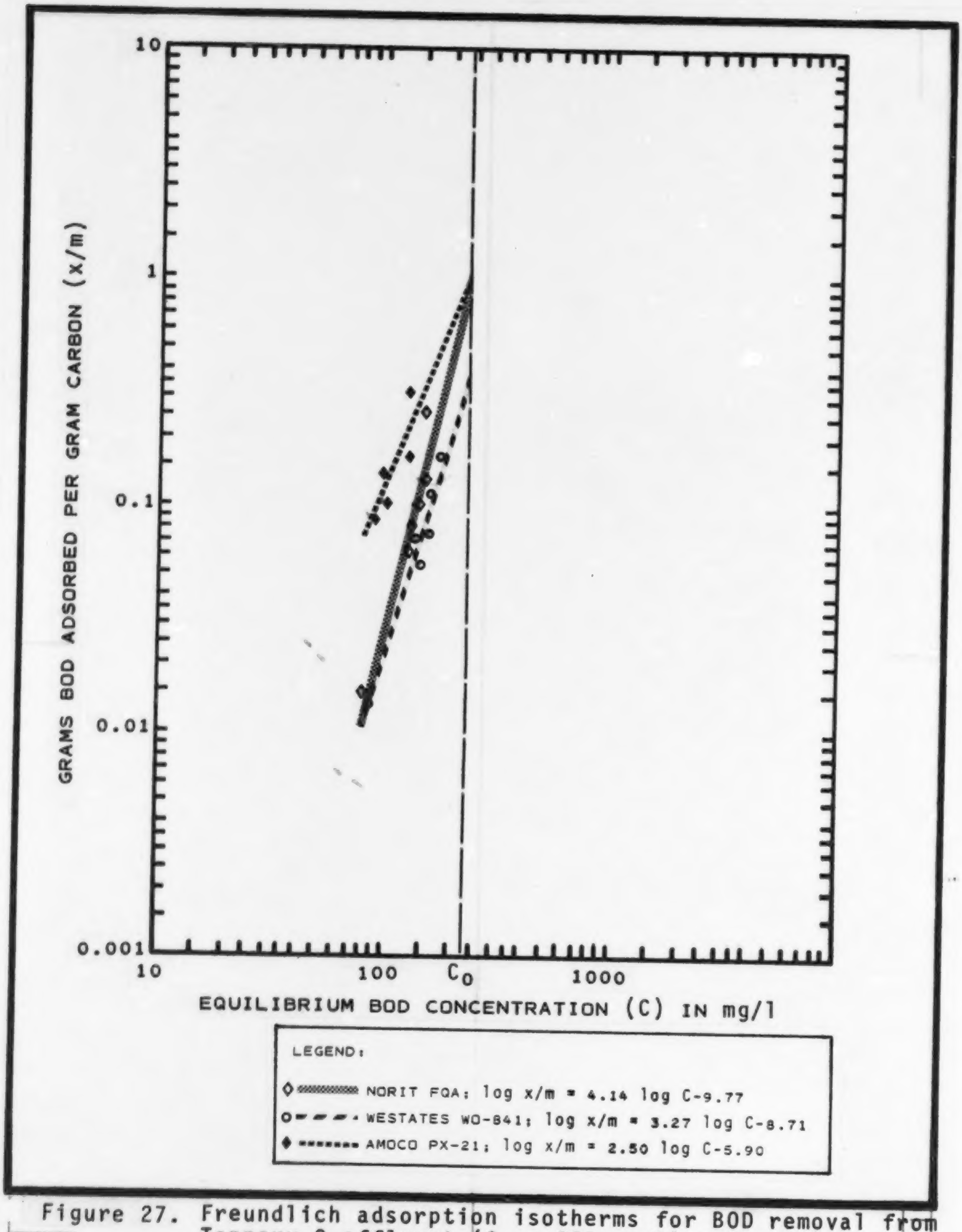

Figure 27. Freundlich adsorption isotherms for BOD removal from Tannery O effluent (C_0 = 228 mg/l) using Norit FQA, Westates WO-841, and Amoco PX-21 carbons.

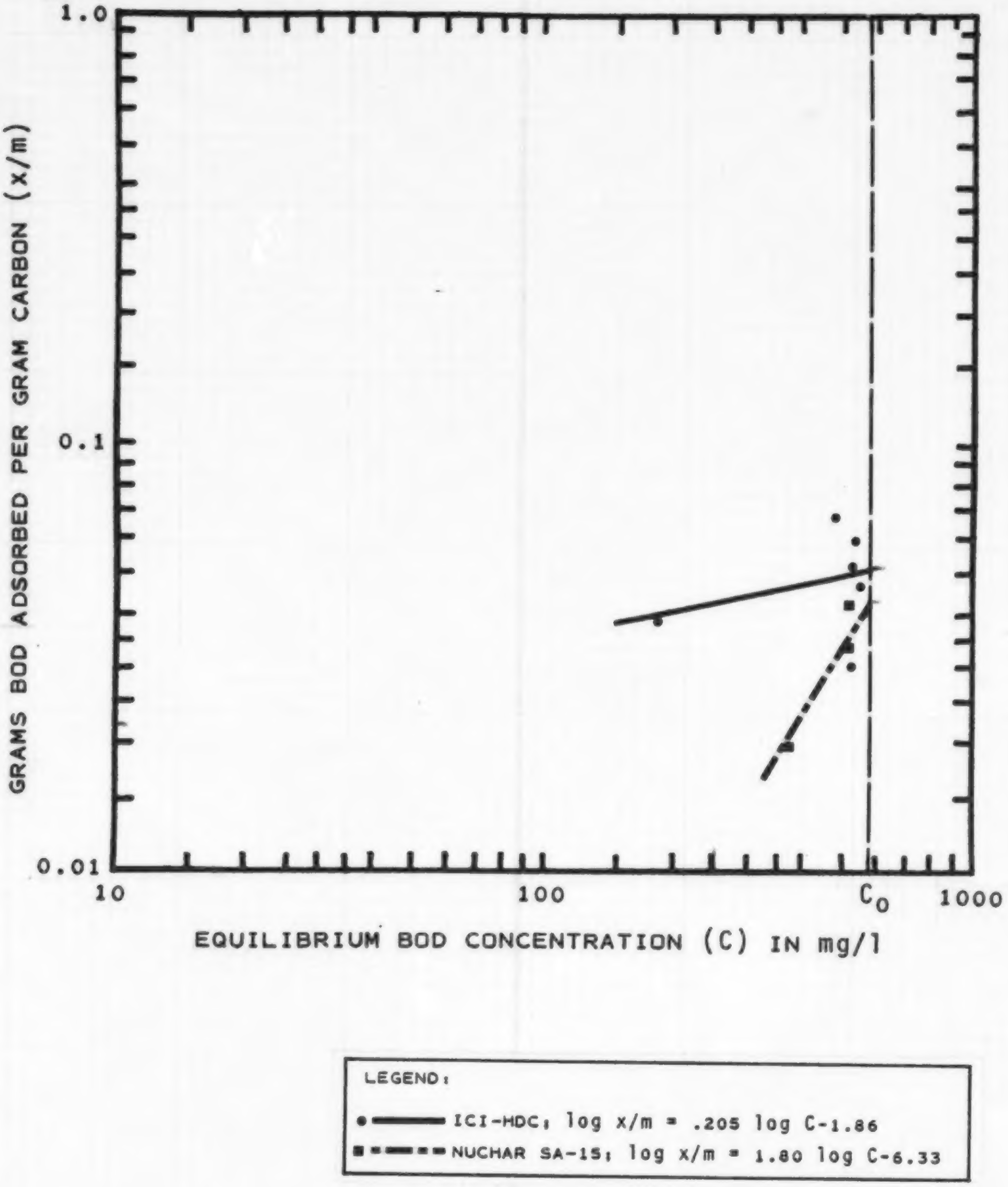

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Figure 28. Freundlich adsorption isotherms for BOD removal from Tannery 4 effluent (C_0 = 574 mg/l) using ICI-HDC and Nuchar SA-15 carbons.

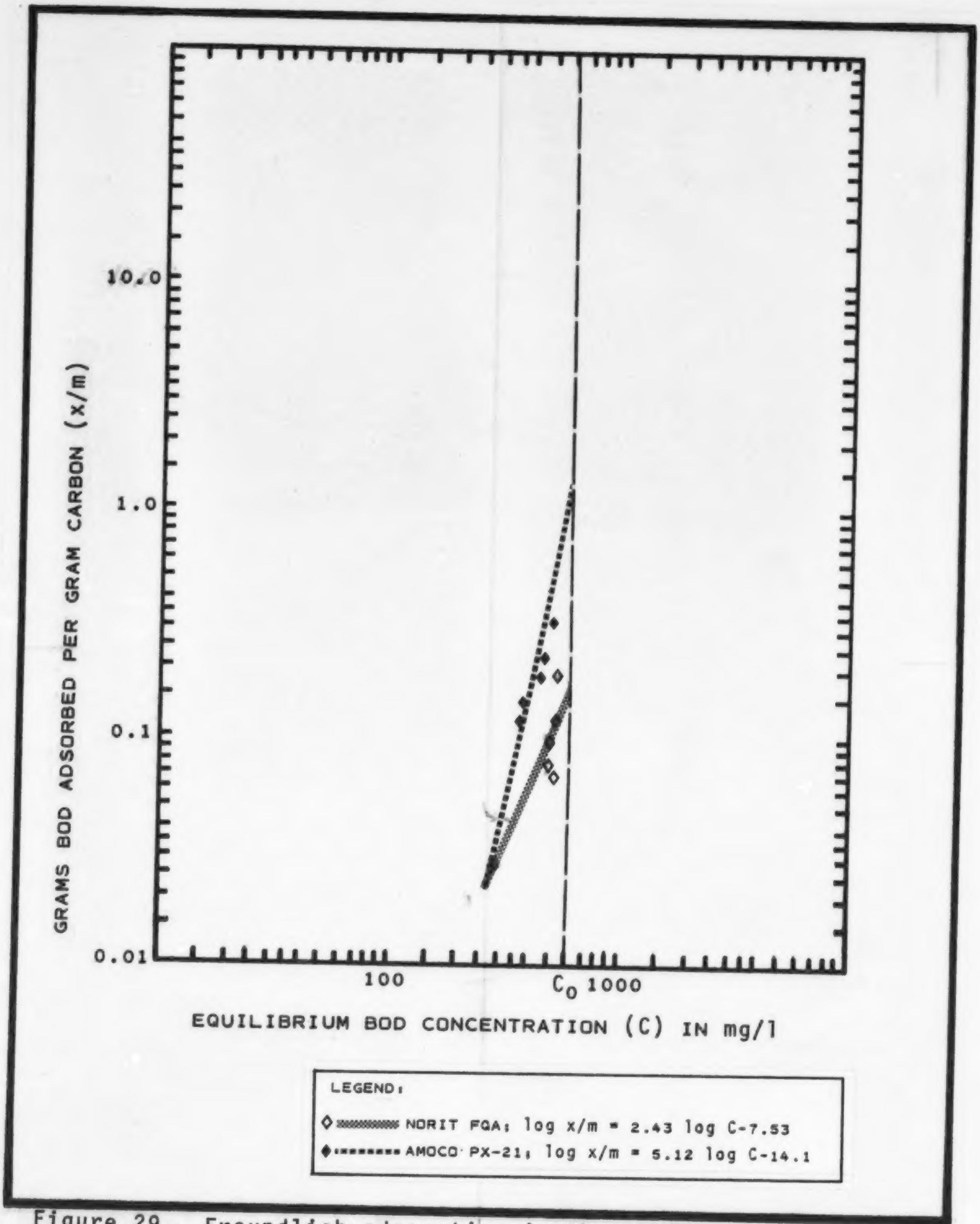

Figure 29. Freundlich adsorption isotherms for BOD removal from Tannery 4 effluent (C_0=574 mg/l) using Norit FQA and Amoco PX-21 carbons.

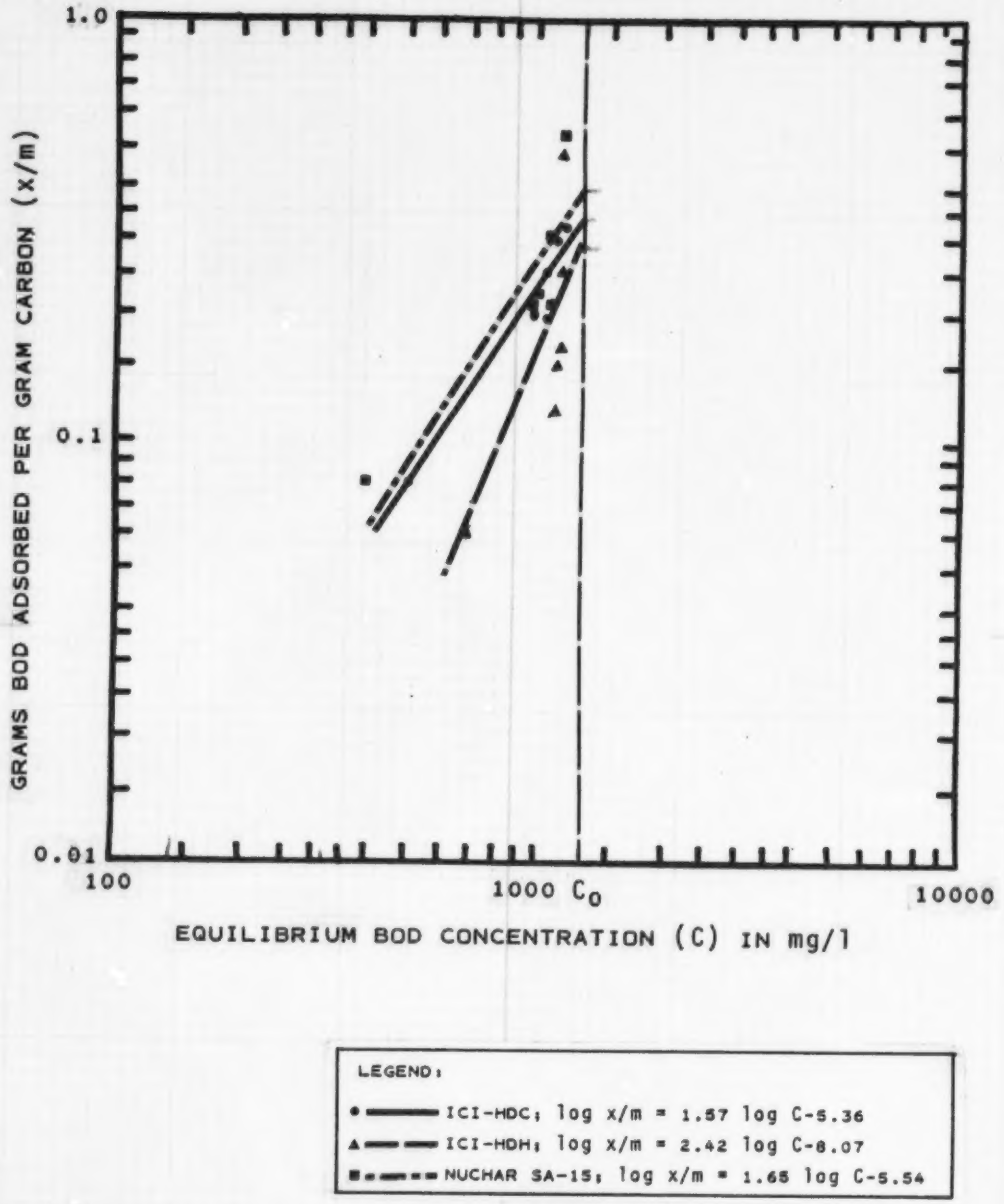

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Figure 30. Freundlich adsorption isotherms for BOD removal from Tannery 9 effluent (C_0 = 1,300 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

Tannery 6

Tannery 6 effluent was found to contain 1,920 mg/l BOD. The three carbons tested for the removal of BOD-contributing compounds exhibited marked differences. Nuchar SA-15 showed an increase in BOD removal as a function of carbon dose, ranging from 27 to 63 percent for doses of 0.3 to 1.5 g/l, respectively (Table 9). The ultimate capacity of this carbon was estimated from the experimental data (Figure 31) to be approximately 2.4 g BOD/g carbon. The other extreme was ICI-HDC carbon, which was essentially ineffective when applied in a dose range of 0.3 to 1.5 g/l; its ultimate capacity was estimated to be less than 0.03 g BOD/g carbon. ICI-HDH carbon was found to be more effective than ICI-HDC; its BOD removal efficiencies at carbon doses of 0.3 to 1.5 g/l ranged from 3 to 11 percent. Its ultimate capacity was estimated to be 0.2 g BOD/g carbon (Figure 31), approximately one order of magnitude lower than for Nuchar SA-15.

Tannery 3

Experimental results on BOD removals from the effluent generated by Tannery 3 (988 mg/l) indicated that ICI-HDH carbon was essentially ineffective within the range of carbon doses from 0.3 to 1.5 g/l (1 to 5 percent removal) (Table 9). Nuchar SA-15 and ICI-HDC, however, showed an increase in BOD removal efficiencies from 4 to 13 percent, and 3 to 10 percent, respectively. These data indicated the following ultimate capacities for removal of BOD from this effluent: ICI-HDC, 0.09; ICI-HDH, 0.04; and Nuchar SA-15, 0.16 g BOD/g carbon (Figure 32 and Table A-8).

Tannery 8

Experimental results revealed that Nuchar SA-15 appeared to be the most effective of the three carbons tested. Nuchar SA-15 exhibited a constant increase in BOD removal as a function of its concentration, ranging from 21 to 58 percent for doses of 0.3 and 1.5 g/l, respectively (Table 9). For ICI-HDC carbon, however, BOD removal efficiencies ranged from 8 to 33 percent for doses of 0.3 and 1.5 g/l, respectively, while ICI-HDH carbon exhibited the lowest efficiency in the same dose range (3 to 15 percent). With respect to the BOD content of this particular tannery effluent, the saturation capacities for all three carbons were estimated to be in the range of 0.09 to 0.9 g BOD/g carbon (Figure 33).

Tannery 2

In the experimental range investigated, ICI-HDC and ICI-HDH were found to be essentially ineffective for BOD removal from Tannery 2 effluent, not exceeding more than approximately 7 to 8 percent removal in the range of 0.3 to 1.5 g/l (Table 9). Nuchar SA-15, however, removed 12 to 36 percent BOD within the same range (Table 9). Ultimate capacities of these three carbons were thus estimated to be approximately 0.04, 0.05, and 0.4 g BOD/g carbon, respectively (Figure 34 and Table A-10).

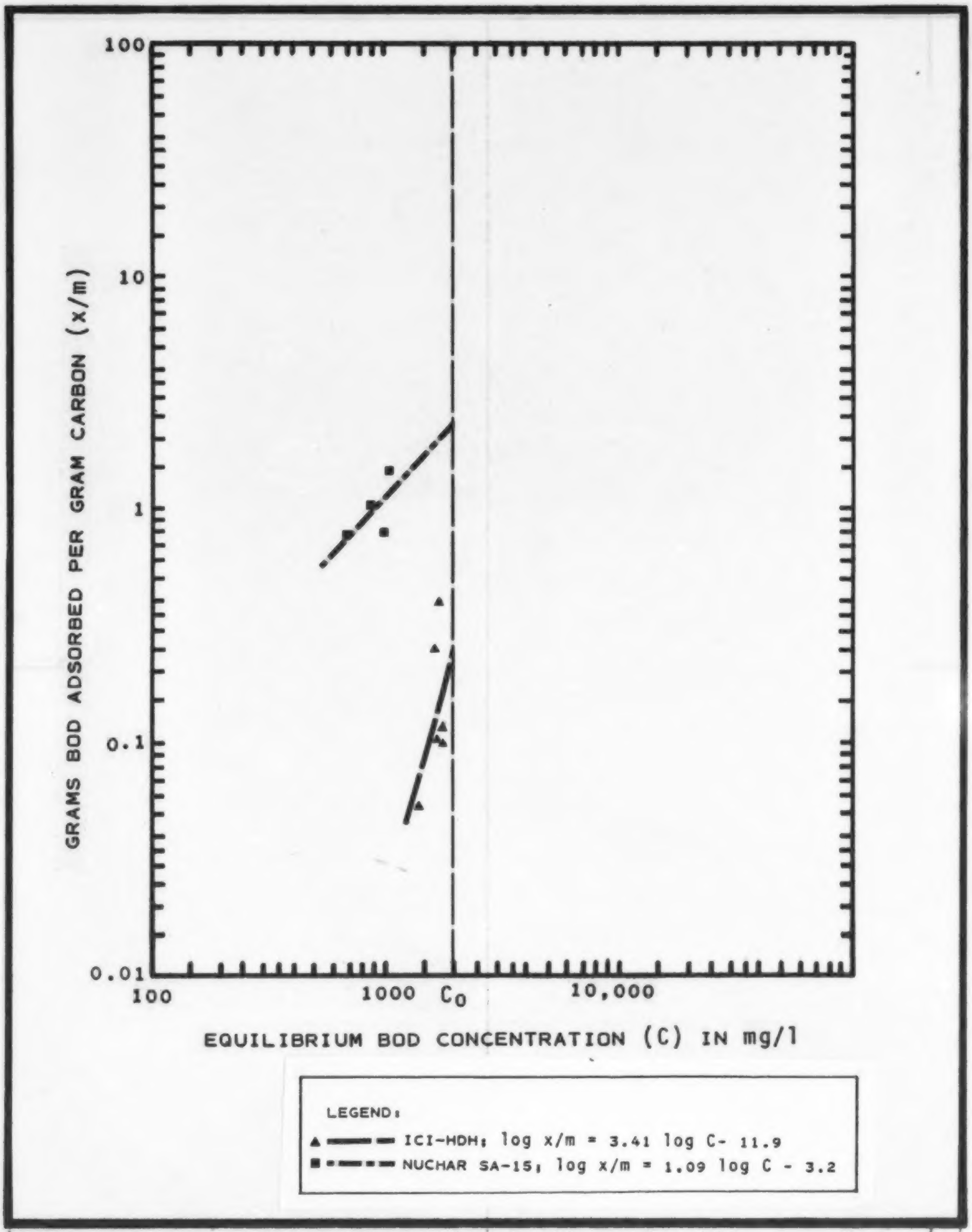

Figure 31. Freundlich adsorption isotherm for BOD removal from Tannery 6 effluent (C_0 = 1,920 mg/l) using ICI-HDH and Nuchar SA-15 carbons.

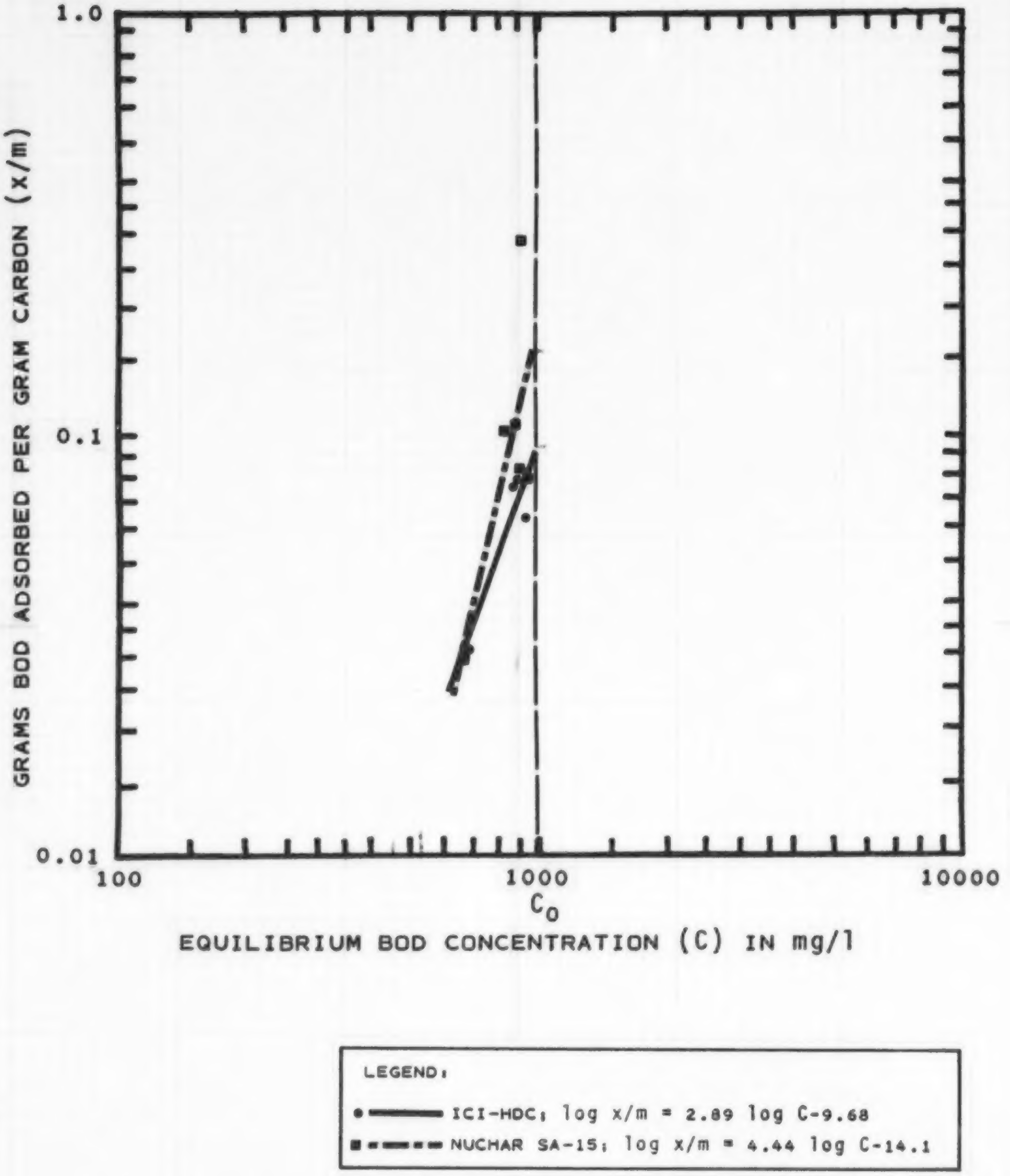

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Figure 32. Freundlich adsorption isotherms for BOD removal from Tannery 3 effluent (C_0 = 988 mg/l) using ICI-HDC and Nuchar SA-15 carbons.

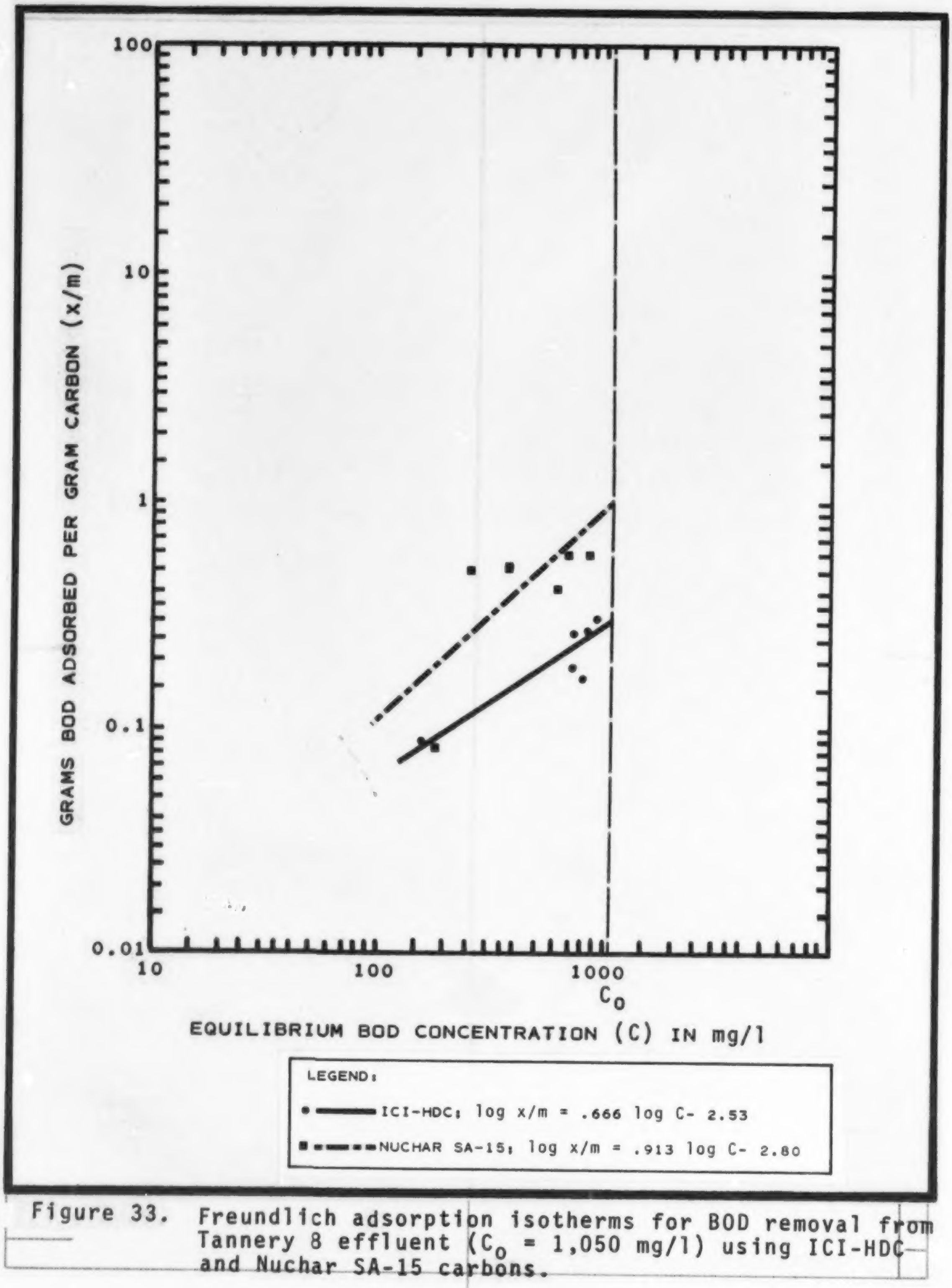

Figure 33. Freundlich adsorption isotherms for BOD removal from Tannery 8 effluent (C_0 = 1,050 mg/l) using ICI-HDC and Nuchar SA-15 carbons.

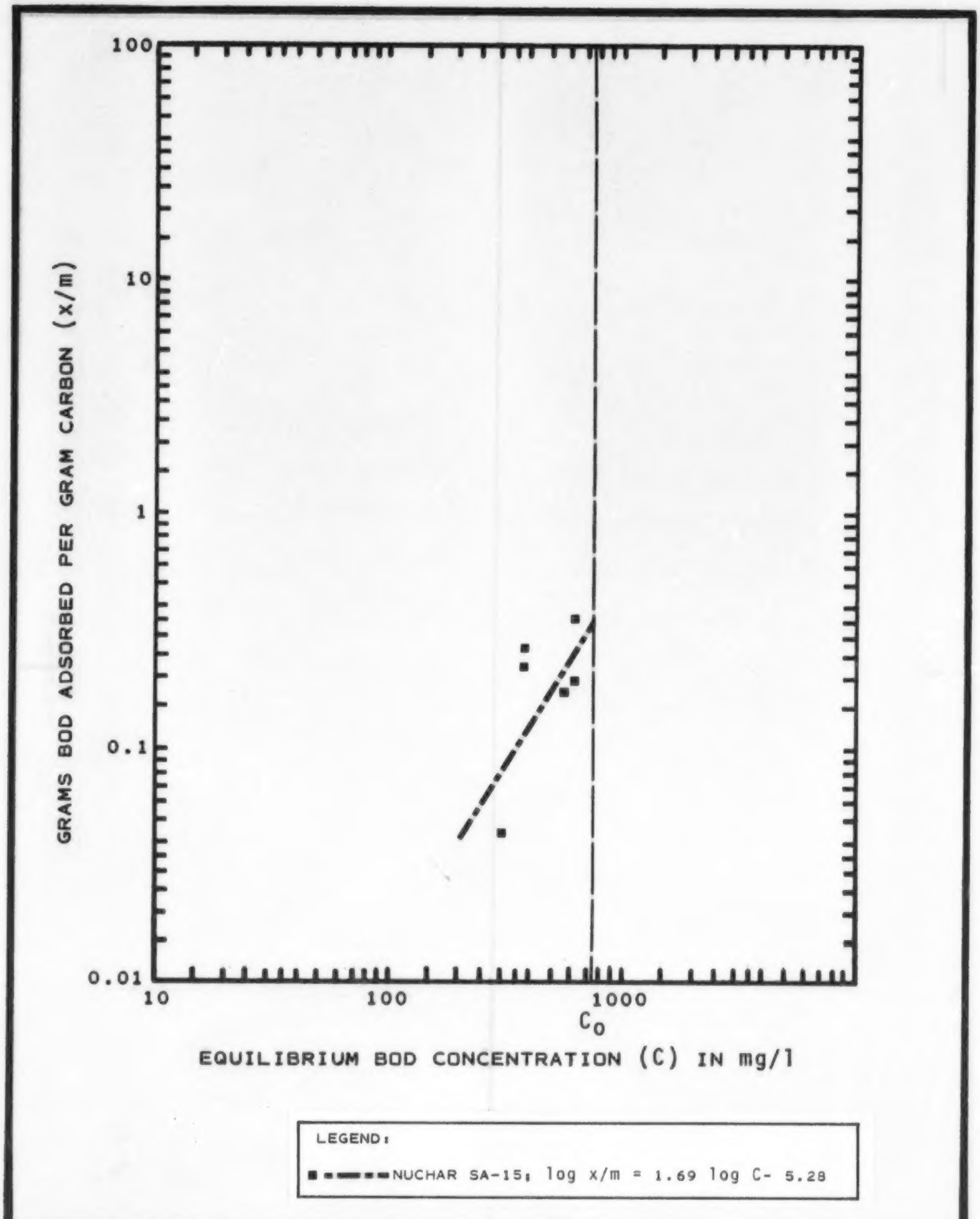

Figure 34. Freundlich adsorption isotherm for BOD removal from Tannery 2 effluent (C_0 = 738 mg/l) using Nuchar SA-15 carbon.

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Tannery 7

Tannery 7 effluent was found to contain the highest concentration of BOD-contributing compounds (i.e., 16,200 mg/l); all tests were thus performed using a 1:10 dilution of this effluent. Nuchar SA-15 was effective in removing 18 percent BOD when added to the diluted tannery effluent at a dose of 0.3 g/l; 26 percent when added at a dose of 0.6 g/l; and 39 percent at a dose of 1.5 g/l. ICI-HDC and ICI-HDH were found to be less effective, each removing 11, 17, and 26 percent BOD at the above respective carbon doses (Table 9). Ultimate capacities of these carbons were estimated to be approximately 1 g BOD/g carbon (Figure 35).

Tannery 5

The effectiveness of the three carbons tested for BOD removal from Tannery 5 effluent (590 mg/l) was found to be in the following descending order: Nuchar SA-15, ICI-HDC, and ICI-HDH (Table 9 and Figure 36). Nuchar SA-15 removed approximately 27 percent BOD at a 0.3 g/l carbon dose, and 49 percent at 1.5 g/l (Table 9). Its ultimate capacity for BOD removal of Tannery 5 effluent was estimated to be approximately 1 g BOD/g carbon. ICI-HDC and ICI-HDH removed 10 to 28 percent and 3 to 15 percent BOD, respectively, in the above carbon dose range (Table 9). Their ultimate capacities were estimated to be approximately 0.3 to 0.07 g BOD/g carbon, respectively (Figure 36).

SPECIFIC PHENOLS

Four specific chlorophenols were considered in these investigations: 2,4-dichlorophenol, 2,4,5-trichlorophenol, tetrachlorophenol, and pentachlorophenol. Their presence and removal by PAC sorption were examined for two tanneries only.

Analyses of the waste streams generated by Tannery 5 revealed the presence of only 2,4-dichlorophenol (0.38 mg/l), and another phenolic compound, possibly 2,4,5-trichlorophenol (10 mg/l); tetrachlorophenol and pentachlorophenol were not detected (see Table 10). Equilibration of this effluent with different doses of ICI-HDC and Nuchar SA-15 carbons (i.e., 0.3 to 0.9 g/l) resulted in 76 to 87 percent removals of these compounds. Removals with 0.3 g/l ICI-HDH were slightly lower (i.e., 62 percent), but at a dose of 0.9 g/l, removals were essentially the same as with the two other carbons. All three carbons, when added at a dose of 0.9 g/l, also accomplished 94 to 99 percent removal of another phenolic compound, tentatively identified as 2,4,5-trichlorophenol.

In the case of Tannery 7, analyses revealed ambiguous results. Namely, only 2,4-dichlorophenol was detected, but not in any consistent pattern (see Table 11).

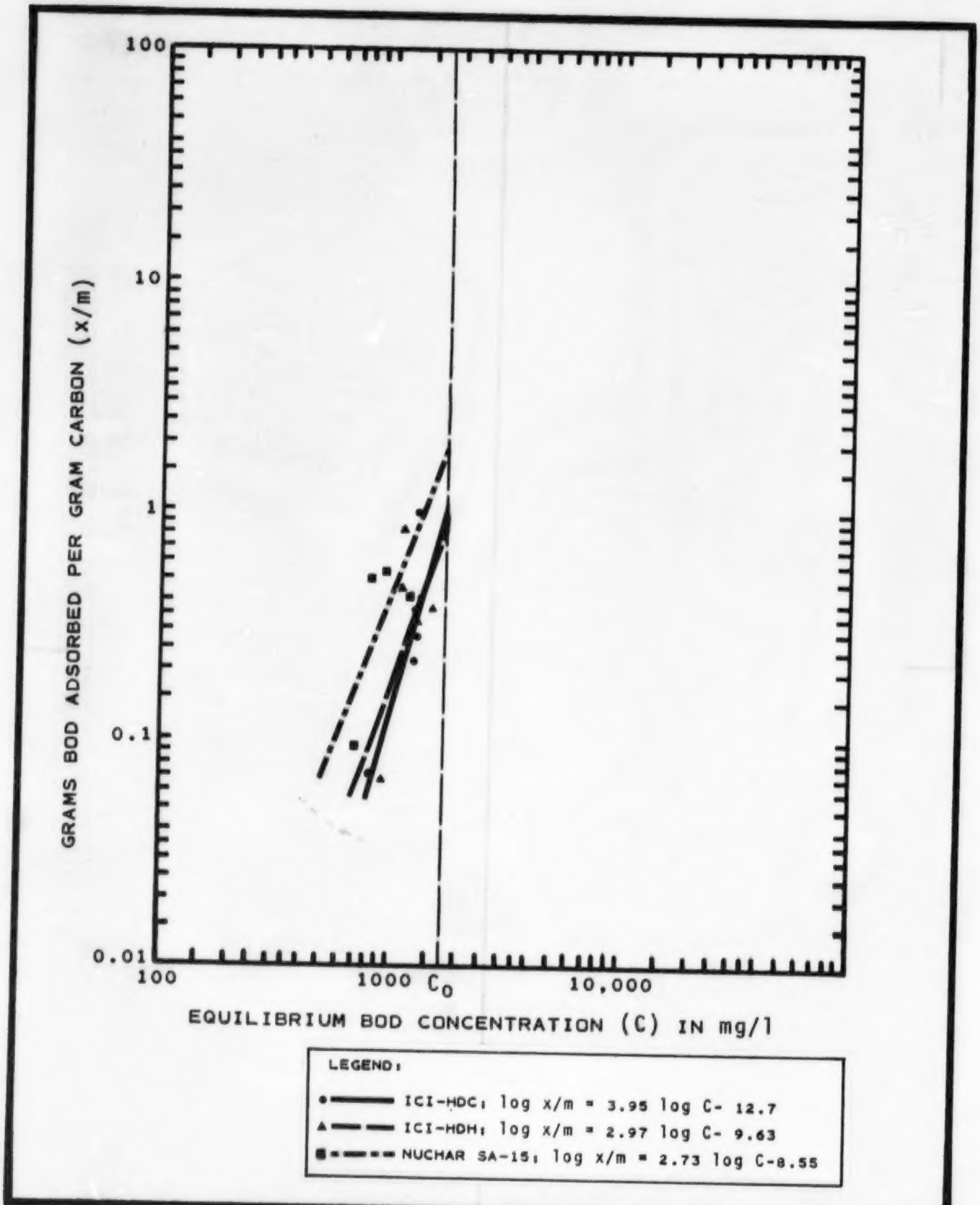

Figure 35. Freundlich adsorption isotherms for BOD removal from tenfold dilution of Tannery 7 effluent (C_0 = 1,620 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

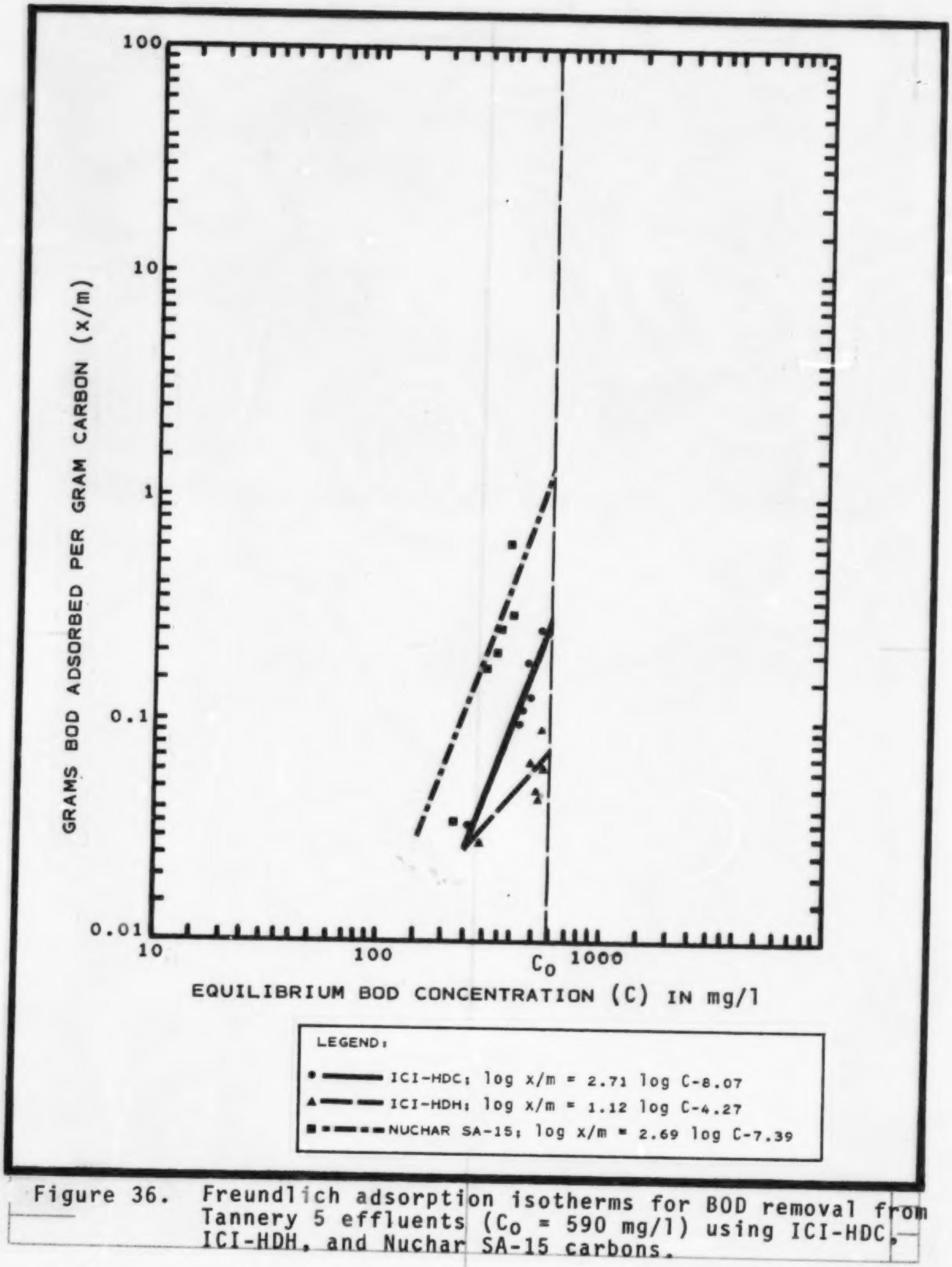

Figure 36. Freundlich adsorption isotherms for BOD removal from Tannery 5 effluents (C_0 = 590 mg/l) using ICI-HDC, ICI-HDH, and Nuchar SA-15 carbons.

TABLE 10. CONCENTRATIONS OF SPECIFIC PHENOLS IN TANNERY 5 EFFLUENT PRIOR TO AND AFTER TREATMENT WITH PAC'S

Carbon Type	PAC Dose (g/l)	2,4-Dichlorophenol (mg/l)	Other Phenolic Compound* (mg/l)
None	0	0.38	10
ICI-HDC	0.3	0.066	1
	0.6	0.08	-
	0.9	0.052	0.6
ICI-HDH	0.3	0.14	-
	0.6	0.118	0.3
	0.9	0.065	0.3
Nuchar SA-15	0.3	0.09	3
	0.6	0.089	-
	0.9	0.052	0.1

* Possibly 2,4,5-trichlorophenol.

TABLE 11. CONCENTRATIONS OF 2,4-DICHLOROPHENOL (mg/l) IN TANNERY 7 EFFLUENT PRIOR TO AND AFTER TREATMENT WITH PAC'S

	PAC Dose (g/l)						
Carbon Type	0	0.3	0.6	0.9	1.2	1.5	10.0
ICI-HDC	0.03*	-	0.31	-	0.31	-	-
ICI-HDH	-	0.15	0.29	-	-	0.32	0.12
Nuchar SA-15	-	0.12	0.18	0.11	0.19	0.19	-

* Detected as 2,4,5-trichlorophenol.

The control sample showed traces of 2,4,5-trichlorophenol, but no 2,4-dichlorophenol. These erratic results may be a function of this particular waste, a very thick, greenish effluent with a COD value of 39,600 mg/l.

Based on the above experimental results, it can be concluded that, within the carbon dose range studied, all three carbons essentially removed most of the identified specific phenols in the effluent from Tannery 5, but had no observable effect on the effluent from Tannery 7.

TOC

Equilibrium data for carbon adsorption of organic constituents contained in tannery effluents (measured cumulatively and expressed in terms of TOC) are presented in Tables A-1 through A-12 (Appendix A). Examination of the quantities of adsorbed TOC suggested that, within the range of carbon doses studied, the observed TOC removals, in most cases, appeared either to be approaching or were at the saturation capacities for each carbon tested. In general, accountable decreases in TOC concentrations were observed only at high carbon doses (i.e., 10 g/l), indicating low efficiencies by all three carbons for the removal of TOC from all effluents tested.

CHROMIUM

Many researchers (6, 7, 8, 9, 10, 11, 12, 13) have observed that chromium is most effectively adsorbed on activated carbon in an acidic environment; adsorption density increases exponentially with decreasing pH. Often, the percentage of chromium removal is also greatly affected by the total concentration of chromium and its chemical speciation, and by the relative concentrations of chromium and carbon surface.

Examination and screening of the experimental results of this study with ICI carbons and Nuchar SA-15 (presented in Appendix A) indicated that, in general, equilibration of effluents from Tanneries 1, 2, and 8, with both low and high carbon doses, resulted in low chromium removals (0 to 37 percent, 0 to 50 percent, and 0 to 5 percent, respectively). pH measurements, performed on nontreated effluents as well as after every treatment (see Table A-1), showed that the above effluents were characterized by high pH values (10 to 12); these values may be an explanation for the apparent low chromium adsorption even at high carbon doses. On the other hand, Tannery 3 effluent (characterized by low pH values of approximately 4) exhibited up to almost 90 percent chromium removals when equilibrated with 10 g/l carbon doses. Similarly, the observed chromium removals from Tannery 0 effluent may also be explained by suspension pH. Namely, pH values, ranging from approximately 6 to 8, were higher than those measured for Tannery 3, but lower than those for Tanneries 1, 2, and 8 (Table A-13). The observed chromium removals at 10 g/l (approximately 60 to 70 percent) (Table A-11) were higher than those measured for Tanneries 1, 2, and 8, but lower than for Tannery 3, thus corresponding to the pH trend.

Effluents from Tanneries 4, 5, 7, and 9 were characterized by high pH values (approximately 9, 11, 11.5, and 12, respectively) (Table A-13). Nevertheless, more than 50 percent chromium removals were observed. Since there is no information available on detailed chemical characterization of these effluents, no specific interpretation of the observed chromium removals can be offered at this point.

OIL AND GREASE

Measurements of oil and grease concentrations in tannery effluents both before and after equilibration with activated carbons generally indicate that, within the range tested, the above carbons were inefficient in the removal of oil and grease.

SECTION 6

ESTIMATED COSTS OF PAC ADDITION TO BIOLOGICAL TREATMENT OF TANNERY WASTEWATER

The addition of PAC to activated sludge systems treating leather tanning wastes is a possible method for upgrading the performance of the treatment system. If PAC addition proves to be technically feasible and effective, economic considerations must then be considered.

The rate of carbon addition to the biological treatment system will be a function of its cost and the effectiveness of the carbon in pollutant removal. These two factors provide a range of carbon addition rates: an upper bound based on prohibitive costs, and a lower bound based on lack of effectiveness. For the purposes of this study, an upper bound of 10 g/l and a lower bound of 300 mg/l have been selected.

The following assumptions are made in estimating the cost of carbon addition:

- Carbon is assumed to cost $0.50/lb delivered to the treatment plant.
- Equipment cost is assumed to be negligible. This assumption is based on the fact that carbon addition does not have to be continuous or carefully monitored. Manual addition is possible for small systems, with dosages simply a function of flow rate.
- Sludge disposal costs are not included. These costs are site-specific, and the increase in volume of sludge due to carbon addition is not clear. The addition of PAC may inprove the dewatering characteristics of the sludge, and thus may not significantly increase the volume requiring disposal as would normally be anticipated.
- Aeration rates in the activated sludge tank are assumed to be sufficient to maintain the suspension of the increased solids load in the basin.

Under these assumed conditions, the cost of treatment with PAC results from both the cost of the carbon and the labor required for its addition to the aeration basin. If a flow of

100,000 gal/day is assumed, the carbon requirement (in lb/day) is as follows: 100,000 gal/day x 3.785 l/gal x 0.001 g/mg x 2.2 x 10^{-3} lb/g x carbon dose (in mg/l).

To achieve a concentration of 100 mg/l in the wastewater, the addition of 85 lb/day of carbon would be required at the seasonal flow of 100,000 gal/day. At the assumed cost of $0.50/lb, a tannery discharging 100,000 gal of effluent per day would spend about $125 per day to achieve a carbon dose of 300 mg/l. Higher carbon doses would be correspondingly more expensive, with the highest dosage, 10 g/l, costing in excess of $4,250 per day in carbon alone.

SECTION 7

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APPENDIX A

EXPERIMENTAL RESULTS

TABLE A-1. REMOVAL OF POLLUTANTS FROM TANNERY O EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	410	345	16	305	26	255	38	220	46	195	52	95	77
BOD	228	108	53	101	56	85	63	70	69	72	68	33	86
TOC	182	172	5	120	34	110	40	104	43	64	65	63	65
Phenol#	27.3	18.2	33	13.5	51	10.5	62	8.4	69	6.4	77	4.3	84
Cr (Total)	0.86	0.55	36	0.4	54	0.32	63	0.3	65	0.38	56	0.36	58
O&G**	60	26	57	48	20	156	--	112	--	16	73	52	13
ICI-HDH													
COD	410	385	6	335	18	290	29	265	35	230	44	135	67
BOD	228	118	78	112	51	105	53	92	60	94	59	49	79
TOC	182	172	5	180	--	126	31	120	34	138	24	72	60
Phenol	27.3	19.5	29	14.7	46	11.2	59	11.4	58	9.8	64	2.9	89
Cr (Total)	0.86	0.73	15	0.68	21	0.61	29	0.28	68	0.03	94	0.37	57
O&G	60	32	47	26	57	22	63	24	60	22	63	16	73
NUCHAR SA-15													
COD	410	285	30	225	45	195	52	180	56	170	59	(135)††	(67)
BOD	228	123	46	114	50	112	51	124	46	141	38	104	54
TOC	182	120	34	100	45	100	45	108	--	80	56	82	55
Phenol	27.3	13.8	51	9.3	66	6.7	75	5.6	79	4.4	84	0.8	97
Cr (Total)	0.86	0.3	65	0.25	71	0.23	73	0.14	84	0.23	73	0.25	71
O&G	60	14	77	38	37	6	90	34	43	26	57	52	13

* FC = Final Concentration (mg/l).

† PR = Percent Removal = FC/Initial Concentration.

Total hydroxylated aromatics expressed as phenol.

** O&G = Oil and Grease.

†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

Determined on aerated control (blank).

TABLE A-2. REMOVAL OF POLLUTANTS FROM TANNERY O EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
NORIT FQA													
COD	410	325	21	295	28	235	43	225	45	205	50	90	78
BOD	228	150	34	146	36	134	41	128	44	128	44	82	64
TOC	182	136	25	140	23	140	23	84	54	100	45	60	67
Phenol#	27.3	19.4	29	17.7	35	14.3	48	11.3	59	10.3	62	0.6	98
Cr (Total)	0.86	0.25	70	0.1	88	0.13	85	0.06	93	0.06	93	0.11	87
O&G**	60	48	20	46	23	46	23	52	13	46	23	46	23
WESTATES WO-841													
COD	410	380	7	370	10	350	15	330	20	315	23	175	57
BOD	228	178	22	162	29	158	31	142	38	145	36	87	62
TOC	182	180	1	156	14	164	10	128	30	136	25	100	45
Phenol	27.3	24.8	9	23.9	12	21.7	21	19.4	29	19	30	6.9	75
Cr (Total)	0.86	1.1	--	0.8	7	0.7	19	0.6	30	0.6	30	0.7	19
O&G	60	40	33	42	30	46	23	40	33	48	20	38	37
AMOCO PX-21													
COD	410	265	35	240	41	204	50	200	51	160	61	90	78
BOD	228	127	44	128	44	99	57	98	57	88	61	(67)††	(71)
TOC	182	140	23	120	34	116	36	108	41	84	54	80	56
Phenol	27.3	13.7	50	9.8	64	6.8	75	5.8	79	4.8	82	0.2	99
Cr (Total)	0.86	0.35	60	0.22	75	0.42	51	0.33	62	0.4	54	0.22	75
O&G	60	36	40	40	33	26	57	36	40	34	43	36	40

* FC = Final Concentration (mg/l).
† PR = Percent Removal = FC/Initial Concentration.
# Total hydroxylated aromatics expressed as phenol.
** O&G = Oil and Grease.
†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.
Determined on aerated control (blank).

TABLE A-3. REMOVAL OF POLLUTANTS FROM TANNERY 4 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

Carbon/Parameter	Initial Concentration[##] (mg/l)	PAC Dose (g/l) 0.3		0.6		0.9		1.2		1.5		10.0	
		FC[*]	PR[†]	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	854	(836)[††]	2	754	13	745	13	654	23	591	31	409	52
BOD	574	560	2	538	6	527	8	493	14	529	78	182	68
TOC	375	300	20	325	13	305	19	245	35	260	31	140	63
Phenol[#]	49.6	50	--	46	7	45.2	9	47.2	5	45.6	8	28	44
Cr (Total)	3.75	6.4	--	7.2	--	6.9	--	2.8	25	6.9	--	0.8	79
O&G[**]	94	76	19	84	11	76	19	68	28	72	23	68	28
ICI-HDH													
COD	854	872	--	909	--	(763)	(11)	763	11	655	23	373	56
BOD	574	742	--	622	--	631	--	641	--	602	--	317	45
TOC	375	310	17	308	18	292	22	275	27	280	25	147	61
Phenol	49.6	49.4	--	55.2	--	56	--	46	7	48	3	29	42
Cr (Total)	3.75	2.2	41	1.9	49	1.5	60	2	47	2.6	31	1.5	60
O&G	94	92	2	97	--	86	9	90	4	93	1	85	10
NUCHAR SA-15													
COD	854	664	22	618	28	564	34	545	36	455	47	(400)	(53)
BOD	574	638	--	683	--	584	--	524	9	524	9	371	35
TOC	375	280	25	340	9	230	39	225	40	212	43	150	60
Phenol	49.6	49.6	--	47.6	4	44	11	40	19	42	15	28	44
Cr (Total)	3.75	3.5	7	3.5	7	3.4	9	3.4	9	3.4	9	--	--
O&G	94	98	--	78	17	24	74	58	38	18	81	15	84

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[*] FC = Final Concentration (mg/l).

[†] PR = Percent Removal = FC/Initial Concentration.

[#] Total hydroxylated aromatics expressed as phenol.

[**] O&G = Oil and Grease.

[††] Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

[##] Determined on aerated control (blank).

TABLE A-4. REMOVAL OF POLLUTANTS FROM TANNERY 4 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

Carbon/Parameter	Initial Concentration## (mg/l)	PAC Dose (g/l) 0.3 FC*	0.3 PR†	0.6 FC	0.6 PR	0.9 FC	0.9 PR	1.2 FC	1.2 PR	1.5 FC	1.5 PR	10.0 FC	10.0 PR
NORIT FQA													
COD	854	931	--	(851)††	(0.4)	812	5	792	7	752	88	455	47
BOD	574	516	10	503	12	483	16	487	15	484	16	285	50
TOC	375	340	9	338	10	312	17	290	23	230	39	170	55
Phenol#	49.6	68	--	68	--	67	--	56	--	59	--	13	74
Cr (Total)	--	--	--	--	--	--	--	--	--	--	--	--	--
O&G**	94	22	77	20	79	28	70	28	70	26	72	20	79
WESTATES WO-84													
COD	854	1,069	--	1,010	--	1,050	--	1,030	--	1,070	--	752	12
BOD	574	573	--	558	3	537	6	570	1	613	7	570	1
TOC	375	350	7	300	20	330	12	270	28	360	4	350	7
Phenol	49.6	62	--	68	--	62	--	67	--	69	--	66	--
Cr (Total)	--	--	--	--	--	--	--	--	--	--	--	--	--
O&G	94	38	60	26	72	30	68	34	64	32	66	34	64
AMOCO PX-21													
COD	854	634	26	544	36	535	37	495	42	455	47	297	65
BOD	574	480	16	432	25	405	29	398	31	380	34	298	48
TOC	375	225	4	195	48	190	49	180	52	180	52	130	65
Phenol	49.6	45	9	44	11	41	17	39	21	26	48	8.8	82
Cr (Total)	--	--	--	--	--	--	--	--	--	--	--	--	--
O&G	94	32	66	36	62	34	64	34	64	32	66	22	77

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* FC = Final Concentration (mg/l).

† PR = Percent Removal = FC/Initial Concentration.

# Total hydroxylated aromatics expressed as phenol.

** O&G = Oil and Grease.

†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

## Determined on aerated control (blank).

TABLE A-5. REMOVAL OF POLLUTANTS FROM TANNERY 1 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

Carbon/Parameter	Initial Concentration## (mg/l)	PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
		FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	2,366	2,178	8	2,030	14	1,901	20	1,951	18	1,921	19	(545)††	(77)
BOD	1,381	1,044	24	1,006	27	955	31	857	38	925	33	536	61
TOC	640	400	38	400	38	480	25	370	42	405	37	140	78
Phenol#	179	180	--	175	2	168	6	160	11	153	15	63	65
Cr (Total)	5.4	5.2	4	4.8	11	5.5	--	4.8	11	7.1	--	5	7
O&G**	46	66	--	70	--	40	13	58	--	32	30	34	26
ICI-HDH													
COD	2,366	(1,931)	(18)	1,901	20	1,752	26	1,713	28	1,693	28	822	65
BOD	1,381	1,091	21	1,057	23	1,017	26	1,002	27	1,070	23	622	55
TOC	640	415	35	375	41	320	50	350	45	350	45	250	61
Phenol	179	165	8	183	--	178	1	155	13	158	12	103	42
Cr (Total)	5.4	5.4	--	2.8	48	3.6	33	3.1	43	3.5	35	3.4	37
O&G	46	52	--	40	13	62	--	70	--	26	43	38	17
NUCHAR SA-15													
COD	2,366	(1,891)	(20)	1,782	25	1,832	23	1,584	33	1,564	34	812	66
BOD	1,381	907	34	944	32	947	31	914	34	885	36	614	56
TOC	640	630	2	570	11	500	22	390	39	220	66	220	66
Phenol	179	160	11	163	9	163	9	160	11	160	11	93	48
Cr (Total)	5.4	5.8	--	5.9	--	6.3	--	5.3	2	5.3	2	5.3	2
O&G	46	24	48	60	--	30	35	48	--	48	--	36	22

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* FC = Final Concentration (mg/l).
† PR = Percent Removal = FC/Initial Concentration.
# Total hydroxylated aromatics expressed as phenol.
** O&G = Oil and Grease.
†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.
## Determined on aerated control (blank).

TABLE A-6. REMOVAL OF POLLUTANTS FROM TANNERY 9 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	2,277	2,030	11	2,000	12	1,980	13	1,842	19	1,742	23	792	65
BOD	1,295	1,193	8	1,110	14	1,065	13	1,058	18	990	24	503	61
TOC	730	720	1	720	1	720	1	630	14	630	14	340	53
Phenol#	255	235	8	220	14	215	16	210	18	200	22	50	80
Cr (Total)	1.92	1.15	40	1.35	30	0.38	80	--	100	--	100	0.1	95
O&G**	48	32	33	26	46	28	42	36	25	32	33	26	46
ICI-HDH													
COD	2,277	2,079	9	2,089	8	1,990	13	1,980	13	1,881	17	1,069	53
BOD	1,295	1,148	11	1,140	12	1,140	12	1,110	14	1,117	14	675	48
TOC	730	720	1	680	7	670	8	650	11	665	9	430	41
Phenol	255	230	10	220	14	230	10	225	12	215	16	105	59
Cr (Total)	1.92	1.96	--	2.03	--	2	--	1.95	--	1.93	--	1.98	--
O&G	48	32	33	34	29	36	25	36	25	34	29	30	38
NUCHAR SA-15													
COD	2,277	2,079	9	1,881	17	1,900	17	1,683	26	1,762	23	693	70
BOD	1,295	1,133	13	1,106	15	1,102	15	1,020	21	975	25	480	63
TOC	730	700	4	700	4	670	8	580	21	570	22	350	52
Phenol	255	(245)††	(4)	220	14	220	14	210	18	195	24	50	80
Cr (Total	1.92	0.88	54	0.85	56	0.75	61	0.75	61	0.74	61	0.72	63
O&G	48	32	33	34	29	32	33	32	33	28	42	30	38

* FC = Final Concentration (mg/l).

† PR = Percent Removal = FC/Initial Concentration.

# Total hydroxylated aromatics expressed as phenol.

** O&G = Oil and Grease.

†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

## Determined on aerated control (blank).

TABLE A-7. REMOVAL OF POLLUTANTS FROM TANNERY 6 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	3,465	2,475	29	2,673	23	2,376	31	2,376	31	2,228	35	1,881	46
BOD	1,920	2,016	--	2,036	--	1,896	1	1,926	--	1,873	2	1,336	30
TOC	750	750	--	720	4	700	7	620	17	650	13	470	37
Phenol#	212	192	9	185	13	190	10	188	11	172	19	92	57
Cr (Total)	--	--	--	--	--	--	--	--	--	--	--	--	--
O&G**	68	24	65	20	71	20	71	28	59	34	50	18	74
ICI-HDH													
COD	3,465	2,574	26	2,425	30	2,525	27	2,327	33	2,525	27	1,683	51
BOD	1,920	1,790	48	1,843	4	1,686	12	1,820	5	1,763	8	1,383	28
TOC	750	740	1	730	3	700	7	550	27	600	20	600	20
Phenol	212	200	6	192	9	180	15	182	14	190	10	120	43
Cr (Total)	--	--	--	--	--	--	--	--	--	--	--	--	--
O&G	68	40	41	42	38	28	59	30	56	24	65	34	50
NUCHAR SA-15													
COD	3,465	2,822	19	2,772	20	2,525	27	2,525	27	2,871	17	1,436	59
BOD	1,920	(1,046)††	(45)	1,026	47	886	54	946	51	690	64	(683)	(64)
TOC	750	700	7	630	16	540	28	570	24	650	13	335	55
Phenol	212	200	6	202	5	192	9	178	16	170	20	58	73
Cr (Total)	--	--	--	--	--	--	--	--	--	--	--	--	--
O&G	68	28	59	38	44	28	59	26	62	58	15	28	59

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* FC = Final Concentration (mg/l).

† PR = Percent Removal = FC/Initial Concentration.

Total hydroxylated aromatics expressed as phenol.

** O&G = Oil and Grease.

†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

Determined on aerated control (blank).

TABLE A-8. REMOVAL OF POLLUTANTS FROM TANNERY 3 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	2,089	1,851	11	1,822	13	1,762	16	1,604	23	1,574	25	871	58
BOD	988	995	--	(972)††	(2)	930	6	893	10	872	12	682	31
TOC	820	780	5	720	12	660	20	700	15	540	34	440	46
Phenol#	120	28	77	31	74	28	77	25	79	20	83	11	91
Cr (Total)	12.1	11	9	14	--	11	9	10.3	15	10.3	15	1.4	88
O&G**	24	32	--	20	17	18	25	18	25	18	25	16	33
ICI-HDH													
COD	2,089	1,931	8	1,733	17	1,772	15	1,663	20	1,643	21	891	57
BOD	988	1,025	--	977	1	952	4	957	31	938	5	747	24
TOC	820	687	16	780	5	800	2	720	12	580	29	460	44
Phenol	120	35	71	31	74	27	78	25	79	23	81	14	88
Cr (Total)	12.1	13	--	12.1	--	13.3	--	14	--	6	50	2.3	81
O&G	24	24	--	20	17	16	33	16	33	16	33	18	25
NUCHAR SA-15													
COD	2,089	1,802	14	1,693	19	1,564	25	(1,356)	(35)	1,465	30	861	59
BOD	988	900	9	940	5	913	8	863	13	833	16	688	30
TOC	820	540	34	660	20	740	10	800	2	815	1	520	37
Phenol	120	88	73	57	53	54	55	53	56	48	27	30	75
Cr (Total)	12.1	23	--	18.5	--	15.5	--	14	--	14.5	--	6.5	46
O&G	24	20	17	20	17	20	17	18	25	16	33	18	28

* FC = Final Concentration (mg/l).

† PR = Percent Removal = FC/Initial Concentration

# Total hydroxylated aromatics expressed as phenol.

** O&G = Oil and Grease.

†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

## Determined on aerated control (blank).

TABLE A-9. REMOVAL OF POLLUTANTS FROM TANNERY 8 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration*** (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD##	2,158	1,960	9	1,792	17	1,663	23	1,604	26	1,505	30	475	78
BOD	1,050	935	11	880	16	785	25	835	20	740	30	160	85
TOC	570	500	12	450	21	410	28	400	30	300	47	70	88
Phenol#	26.5	24.4	9	20.8	22	19.7	26	16.9	36	13	51	0.9	97
Cr (Total)	1.86	1.83	2	1.84	1	1.72	8	1.72	8	1.85	1	1.77	5
O&G**	42	26	38	28	33	26	38	28	33	32	24	26	38
ICI-HDH													
COD##	2,158	1,762	18	1,871	13	1,703	21	1,465	32	1,426	34	139	94
BOD	1,050	990	6	1,040	1	990	6	950	17	918	20	170	85
TOC	570	500	12	480	16	450	21	460	19	400	30	65	89
Phenol	26.5	18.9	29	18.9	29	18	32	19.5	26	15.3	42	1.3	95
Cr (Total)	1.86	1.89	--	2.06	--	2.05	--	1.89	--	1.82	2	1.83	2
O&G	42	28	33	34	19	34	19	36	14	38	10	18	57
NUCHAR SA-15													
COD##	2,158	1,773	18	1,293	40	1,040	52	624	71	475	78	(386)††	(82)
BOD	1,050	865	18	683	35	630	4	398	62	260	75	173	84
TOC	570	450	21	300	47	150	74	125	78	110	81	80	86
Phenol	26.5	24.3	8	22	17	22.8	14	16.8	37	12.1	54	2.2	9
Cr (Total)	1.86	1.93	--	1.9	--	1.94	--	1.89	--	1.91	--	1.9	--
O&G	42	24	43	28	33	36	14	34	19	32	24	22	48

* FC = Final Concentration (mg/l).
† PR = Percent Removal = FC/Initial Concentration.
# Total hydroxylated aromatics expressed as phenol.
** O&G = Oil and Grease.
†† Parentheses denote data eliminated from further analysis to obtain correlation coefficient >0.70.
Measured at different time than the remaining parameters.
*** Determined on aerated control (blank).

TABLE A-10. REMOVAL OF POLLUTANTS FROM TANNERY 2 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	1,188	941	21	842	29	891	25	792	33	792	33	198	83
BOD	738	758	--	751	--	723	2	690	6	681	8	411	44
TOC	475	425	11	425	11	405	15	350	26	425	11	200	58
Phenol#	63.8	53	17	43.8	31	34.5	46	18.8	71	17.3	73	4.5	93
Cr (Total)	1.6	1.3	19	1.2	25	1.1	31	1.1	31	1.3	19	1.2	25
O&G**	38	44	--	40	--	40	--	32	16	36	5	30	21
ICI-HDH													
COD	1,188	941	21	891	25	792	33	842	29	792	33	248	79
BOD	738	732	11	725	11	698	5	675	9	704	5	417	43
TOC	475	350	26	350	26	365	23	450	5	350	26	300	37
Phenol	63.8	51.3	20	49.5	22	40.5	37	(55.8)††	(13)	(49.5)	(22)	8	87
Cr (Total)	1.6	2.2	--	2.1	--	2.3	--	1.2	25	1.1	31	0.8	50
O&G	38	34	11	34	11	38	--	30	21	42	--	30	21
NUCHAR SA-15													
COD	1,188	1,069	10	1,040	12	950	20	752	37	742	38	426	64
BOD	738	624	15	624	15	571	23	397	46	406	45	306	59
TOC	475	470	1	350	26	335	29	365	23	250	47	195	59
Phenol	63.8	50	22	47.5	25	43.3	32	37	42	37.3	42	7.8	88
Cr (Total)	1.6	1.4	13	2.7	--	1.3	19	1.7	--	1.3	19	0.8	50
O&G	38	30	21	26	32	24	37	22	42	18	53	16	58

* FC = Final Concentration (mg/l).
† PR = Percent Removal = FC/Initial Concentration.
# Total hydroxylated aromatics expressed as phenol.
** O&G = Oil and Grease.
†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.
Determined on aerated control (blank).

TABLE A-11. REMOVAL OF POLLUTANTS FROM TANNERY 7 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

		PAC Dose (g/l)											
		0.3		0.6		0.9		1.2		1.5		10.0	
Carbon/Parameter	Initial Concentration## (mg/l)	FC*	PR†	FC	PR	FC	PR	FC	PR	FC	PR	FC	PR
ICI-HDC													
COD	2,772	2,574	7	(2,574)††	(7)	2,376	14	2,228	20	2,238	19	(2,376)	(14)
BOD	1,620	1,327	18	1,367	16	1,293	20	1,270	20	1,277	21	846.6	48
TOC	275.0	260.0	5	250.0	9	245.0	11	220.0	20	200.0	27	120.0	56
Phenol#	325.0	275.5	15	(279.5)	(14)	259.0	20	241.0	26	225.5	31	139.5	57
Cr (Total)	30.9	24.9	19	30.9	--	--	--	19.2	38	20.7	33	--	--
O&G**	1,120	1,160	--	840	25	980	13	1,000	11	1,040	7	1,140	7
ICI-HDH													
COD	2,772	2,475	11	2,178	21	2,277	18	2,277	18	2,277	18	2,079	25
BOD	1,620	1,503	7	1,113	31	1,197	26	1,247	23	(1,463)	(10)	940.0	42
TOC	275.0	240.0	13	245.0	11	220.0	20	215.0	22	260.0	5	160.0	42
Phenol	325.0	335.0	--	224.0	31	241.0	26	259.0	20	245.0	25	169.0	48
Cr (Total)	30.9	20.7	33	22.5	27	20.7	33	10.8	65	17.1	45	--	--
O&G	1,120	1,360	--	960	14	1,060	--	1,060	--	1,040	7	1,100	2
NUCHAR SA-15													
COD	2,772	2,525	9	2,406	13	2,475	11	2,277	18	2,277	18	1,980	29
BOD	1,620	(1,093)	(33)	1,017	(37)	1,207	26	936.6	42	853.3	47	706.6	56
TOC	275.0	235.0	15	260.0	5	220.0	20	220.0	20	200.0	27	140.0	49
Phenol	325.0	243.5	25	242.5	25	241.0	26	243.5	25	235.0	28	161.5	50
Cr (Total)	30.9	4.2	86	3.6	88	3.3	89	2.1	93	1.2	96	--	--
O&G	1,120	700	38	820	27	880	21	860	23	900	20	780	30

* FC = Final Concentration (mg/l).

† PR = Percent Removal = FC/Initial Concentration.

# Total hydroxylated aromatics expressed as phenol.

** O&G = Oil and Grease.

†† Parentheses denote data eliminated from analysis to obtain correlation coefficient >0.70.

## Corresponds to 1:10 dilution of Tannery 7 effluent; determined on aerated control (blank).

TABLE A-12. REMOVAL OF POLLUTANTS FROM TANNERY 5 EFFLUENTS BY ADSORPTION ON DIFFERENT POWDERED ACTIVATED CARBONS (PAC)

Carbon/Parameter	Initial Concentration## (mg/l)	PAC Dose (g/l) 0.3 FC*	0.3 PR†	0.6 FC	0.6 PR	0.9 FC	0.9 PR	1.2 FC	1.2 PR	1.5 FC	1.5 PR	10.0 FC	10.0 PR
ICI-HDC													
COD	1,188	990	16	1,089	8	1,089	8	1,089	8	970	18	594	50
BOD	590	510	14	482	18	474	20	453	23	448	24	262	55
TOC	340	280	18	270	21	250	26	290	15	255	25	145	57
Phenol#	55	57.5	--	60	--	55	58	54	2	50	9	27.5	5
Cr (Total)	2.8	0.6	79	0.8	71	0.5	82	0.31	89	0.36	87	0.3	89
O&G**	110	34	69	30	73	36	67	32	71	34	69	32	71
ICI-HDH													
COD	1,188	1,386	--	1,188	0	990	17	1,089	8	1,039	13	643	46
BOD	590	562	5	552	6	548	7	532	10	491	17	286	52
TOC	340	336	1	330	3	300	12	280	18	280	18	150	56
Phenol	55	60	--	62.5	--	55	0	54	2	50	9	29	47
Cr (Total)	2.8	1.7	39	1	64	1.3	54	0.8	71	0.7	75	0.6	79
O&G	110	22	80	24	78	20	82	22	80	20	82	22	80
NUCHAR SA-15													
COD	1,188	1,089	8	(1,188)††	(0)	1,039	13	891	25	990	17	693	42
BOD	590	399	32	399	32	356	40	344	42	310	47	237	60
TOC	340	300	12	290	15	270	21	225	34	222	35	150	56
Phenol	55	60	--	52.5	5	50	9	47.5	14	(30)	(45)	21	62
Cr (Total)	2.8	0.39	86	0.34	88	0.62	78	0.47	83	0.97	65	0.55	80
O&G	110	49	55	50	55	43	61	35	68	59	46	43	61

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* FC = Final Concentration (mg/l).
† PR = Percent Removal = FC/Initial Concentration.
# Total hydroxylated aromatics expressed as phenol.
** O&G = Oil and Grease.
†† Parentheses denote data eliminated from analysis to obtain coefficient >0.70.
## Determined on aerated control (blank).

TABLE A-13. PH VALUES OF TANNERY EFFLUENTS PRIOR TO AND AFTER TREATMENTS WITH DIFFERENT POWDERED ACTIVATED CARBONS

		PAC Dose (g/l)						
Tannery	Carbon Type	0	0.3	0.6	0.9	1.2	1.5	10.0
0	ICI-HDC	6.63	7.09	7.30	7.63	7.85	8.10	9.56
	ICI-HDH	6.63	6.60	6.75	7.08	7.36	7.52	8.42
	Nuchar SA-15	6.63	6.62	6.59	6.49	6.51	6.45	5.44
	Norit FOA	6.63	7.28	7.31	7.38	7.42	7.37	8.37
	Westates WO-841	6.63	6.93	7.12	7.38	7.51	7.64	9.21
	Amoco PX-21	6.63	6.65	6.68	6.69	6.71	6.72	6.14
1	ICI-HDC	11.90	11.95	11.95	11.95	11.95	11.95	11.80
	ICI-HDH	11.90	12.0	12.0	12.0	12.0	12.0	11.90
	Nuchar SA-15	11.90	11.9	11.90	11.90	11.90	11.90	11.70
2	ICI-HDC	10.80	10.4	11.80	11.0	11.0	11.0	11.30
	ICI-HDH	10.80	10.5	10.50	10.60	10.60	10.60	9.80
	Nuchar SA-15	10.80	9.9	10.0	9.80	9.20	9.30	7.50
3	ICI-HDC	4.30	4.40	4.50	4.60	4.80	5.0	8.20
	ICI-HDH	4.30	4.30	4.30	4.50	4.60	4.60	7.20
	Nuchar SA-15	4.30	3.20	3.80	4.30	4.30	4.30	4.40
4	ICI-HDC	9.20	9.30	9.30	9.30	9.30	9.40	10.20
	ICI-HDH	9.20	9.30	9.30	9.20	9.20	9.20	9.40
	Nuchar SA-15	9.20	9.10	9.0	9.0	8.80	8.80	7.20
	Norit FOA	9.20	9.30	9.20	9.25	9.30	9.30	9.35
	Westates WO-841	9.20	9.10	9.20	9.30	9.40	9.40	9.90
	Amoco PX-21	9.20	9.0	9.10	9.10	8.90	8.90	8.15
5	ICI-HDC	10.90	10.80	10.90	11.0	11.0	11.0	11.10
	ICI-HDH	10.90	10.70	10.80	10.80	10.70	10.70	10.50
	Nuchar SA-15	10.90	10.80	10.70	10.50	11.40	10.40	8.80
6	ICI-HDC	9.50	10.80	10.10	11.10	11.05	10.90	11.10
	ICI-HDH	9.50	9.30	9.30	8.90	9.35	9.25	9.20
	Nuchar SA-15	9.50	11.0	11.05	11.0	10.95	10.90	8.75
7	ICI-HDC	11.51	11.55	11.59	11.60	11.60	11.59	11.65
	ICI-HDH	11.51	11.55	11.60	11.59	11.56	11.58	11.59
	Nuchar SA-15	11.51	11.72	11.82	11.78	11.81	11.80	11.49
8	ICI-HDC	11.18	11.13	11.14	11.15	11.16	11.12	11.23
	ICI-HDH	11.18	11.14	11.15	11.09	11.11	11.10	10.91
	Nuchar SA-15	11.18	11.10	11.05	11.07	11.05	11.0	8.09
9	ICI-HDC	11.95	12.10	12.10	12.10	12.10	12.10	12.10
	ICI-HDH	11.95	12.0	12.0	12.0	12.0	12.0	12.0
	Nuchar SA-15	11.95	12.10	12.10	12.10	12.10	12.10	12.10

APPENDIX B

ANALYTICAL TECHNIQUES

APPENDIX B

ANALYTICAL TECHNIQUES

This appendix contains detailed descriptions of analytical techniques used during the course of this study.

COD

COD determinations were carried out using the EPA-approved ampule technique. This technique utilizes 10-ml round-bottomed ampules containing all of the essential reagents for COD digestion. The tops of the ampules were broken, and 2.5-ml samples were added slowly to the contents of the ampules. The ampules were sealed on the Ampulmatic (Oceanography International Corporation), and transferred to an oven (Lab-Line Imperial II) capable of maintaining a temperature of 150°C (±2°C). After a 2-hour digestion period, the contents of the ampules were measured spectrophotometrically at 600 nm (1.54-cm light path), and converted to mg/l COD (from a standard curve). The precision of this technique is ±3 mg/l COD.

THA

Positive total phenolic determinations were obtained using the modified Lowry procedure (Markwell, et al., 1978) which utilizes the following reagents:

- Reagent A: 2% sodium carbonate; 0.4% sodium hydroxide; 0.16% sodium tartrate; 1% sodium dodecylsulfate.
- Reagent B: 4% copper sulfate pentahydrate; 1N Folin phenol reagent; 2N Folin-Ciocalteau reagent (Fisher Scientific); 1:1 with deionized water.

According to this procedure, 100 parts of Reagent A are mixed with 1 part Reagent B to form Reagent C; 1.0 ml of the sample is incubated with 3.0 ml of Reagent C for 10 to 60 minutes at room temperature; 0.3 ml of 1N Folin is then added, mixed, and incubated for 45 minutes at room temperature. Absorbancy is determined at 660 nm, and converted to phenol content (ppm) from a standard curve.

SPECIFIC PHENOLS: METHOD 604

Specific phenols were determined by Method 604 for phenols as follows:

1. Scope and Application

1.1 This method covers the determination of various phenolic compounds. The following parameters may be determined by this method:

Parameter	STORET No.	Parameter	STORET No.
4-Chloro-3-methylphenol	34452	2-Nitrophenol	34591
2-Chlorophenol	34586	4-Nitrophenol	34646
2,4-Dichlorophenol	34601	Pentachlorophenol	39094
2,4-Dimethylphenol	34606	Phenol	34694
4,6-Dinitro-2-methylphenol	34657	2,4,6-Trichlorophenol	34621
2,4 Dinitrophenol	34616		

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

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TABLE ~~I~~

Flame Ionization Gas Chromatography of Phenols

Compound	Retention Time	Detection † Limit (ug/L)
2-Chlorophenol	1.70	2.0
2-Nitrophenol	2.00	2.5
Phenol	3 01	1.4
2,4-Dimethylphenol	4.03	1.7
2 4-Dichlorophenol	4.30	2.1
2,4,6-Trichlorophenol	6.05	5.0
4-Chloro-3-methylphenol	7.50	8.3
2,4-Dinitrophenol	10.00	7.0
4,6-Dinitro-2 methylphenol	10.24	10.0
Pentachlorophenol	12.42	10.0
4-Nitrophenol	24.25	10.0

Column conditions: Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 6 ft long x 2 mm ID glass column with nitrogen carrier gas at 30 ml/min flow rate. Column temperature is 80°C at injection, programmed immediately at 8°C/min to 150°C final temperature.

†Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final extract volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

Summary of Method

2.1 A 1-liter sample of wastewater is acidified and extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Flame ionization gas chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 The method also provides for the preparation of derivatives for electron capture gas chromatography and additional cleanup procedures to aid the analyst in the elimination of interferences.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

4. Apparatus and Materials

4.1 Sampling equipment for discrete or composite sampling.

4.1.1 Grab sample bottle - amber glass, liter or quart volume.

French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps - Threaded to screw on sample bottles. Caps must be lined with Teflon.

4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing or fittings may be used in this system.

4.2 Separatory funnel - 2000 ml, with Teflon stopcock.

4.3 Drying column - A 20 mm ID Pyrex chromatograhic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent) Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - three-ball micro (Kontes K-569001-0219 or equivalent).

4.4.4 Snyder column - two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - extracted, approximately 10/40 mesh.

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4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 2^{\circ}C$). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including both flame ionization and electron capture, detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column - 10 mm ID by 100 mm length, with Teflon stopcock.

4.8 Reaction vial.

5. Reagents

5.1 Preservatives:

5.1.1 Sodium hydroxide - (ACS) 10 N in distilled water.

5.1.2 Sulfuric acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water (1+1), and 1 N.

5.1.3 Sodium thiosulfate - (ACS) Granular.

5.2 Methylene chloride - Pesticide quality or equivalent.

5.3 Sodium sulfate - (ACS) Granular. anhydrous (purified by heating at $400^{\circ}C$ for 4 hrs.).

5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul by dissolving 0.100 grams of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

6. Calibration

6.1 Prepare calibration standards for the flame ionization detector that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 ug/l in the final extract, for example, prepare standards at 10 ug/l, 50 ug/l, 100 ug/l, 500 ug/l, etc. so that injections of 1-5 ul of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatogrphic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using the derivatization cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate the precision of the derivatization and the absence of interferences from the reagents.

7. Quality Control

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 35 mg of sodium thiosulfate per part per million free chlorine per liter. Adjust the sample pH to 1-2, as measured by pH paper, using sulfuric acid. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. Sample Extraction

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the sample pH to 12 with sodium hydroxide.

9.2 Add 60 ml methylene chloride to the sample bottle and shake 30 seconds to rinse the walls. Transfer the solvent into the separtory funnel, and extract the sample by shaking the funnel for one minute with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Discard the methylene chloride layer, and wash the sample with an additional two 60 ml portions of methylene chloride in similar fashion.

9.3 Adjust the aqueous layer to a pH of 1-2 with sulfuric acid.

9.4 Add 60 ml of methylene chloride to the sample and shake for two minutes. Allow the solvent to separate from the sample and collect the methylene chloride in a 250 ml Erlenmeyer flask.

9.5 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20-30 ml methylene chloride to complete the quantitative transfer.

9.7 Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a steaming hot (60-65°C) water bath so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

9.8 Increase the temperature of the hot water bath to 95-100°C. Momentarily remove the Snyder column, add 10 ml of 2-propanol and a new boiling chip and reattach the Snyder column. Pour about 1 ml of 2-propanol into the top of the Snyder column and concentrate the solvent extract as before. Elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 ml of

2 propanol. A 5 ml syringe is recommended for this operation. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 ml 2-propanol to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of 2-propanol. Adjust the extract volume to 1.0 ml. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with flame ionization gas chromatographic analysis. If the sample requires cleanup, proceed to Section 11.

9.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. After correction for sulfuric acid preservative, record the sample volume to the nearest 5 ml.

10. Gas Chromatography - Flame Ionization Detector

10.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by one of these columns is shown in Figure 1. Calibrate the gas chromatographic system daily with a minimum of three injections of calibration standards.

10.2 Inject 2-5 ul of the sample extract using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected in automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.

10.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

10.4 If the peak area measurement is prevented by the presence of interferences, the phenols must be derivatized and analyzed by electron capture gas chromatography.

11. Derivatization and Electron Capture Gas Chromatography

11.1 Pipet a .0 ml aliquot of the 2-propanol to solution of standard or sample extract into a glass reaction vial. Add 1.0 ml derivatization reagent. This is a sufficient amount of reagent to derivatize a solution whose total phenolic content does not exceed 0.3 mg/ml.

11.2 Add about 3 mg of potassium carbonate to the solution and shake gently.

11.3 Cap the mixture and heat it for 4 hours at 80°C in a hot water bath.

11.4 Remove the solution from the hot water bath and allow it to cool.

11.5 Add 10 ml hexane to the reaction vial and shake vigorously for one minute. Add 3.0 ml of distilled, deionized water to the reaction vial and shake for two minutes.

11.10 Inject 2-5 ul of the column fractions using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected in automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

12. Calculations

12.1 Determine the concentration of individual compounds measured by the flame ionization procedure (without derivatization) according to the formula:

$$\text{Concentration, ug/l} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

where A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = volume of extract injected (ul)

V_t = Volume of total extract (ul)

V_s = Volume of water extracted (ml)

12.2 Determine the concentration of individual compounds measured by the derivatization and electron capture procedure according to the following procedure:

12.2.1 From the concentration of the calibration standards that were derivatized with the samples, calculate the amounts, in nanograms, of underivatized phenols that were added as 2-propanol solution (11.1). From the size of the injection into the electron capture gas chromatograph, determine the nanograms of material (calculated as the underivatized phenol) injected onto the column. Compare the detector responses obtained to develop a calibration factor for the chromatographic system, in nanograms of material per area unit.

12.2.2 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, ug/l} = \frac{(A)\ (B)\ (V_t)(10)\ (D)}{(V_i)\ \ (V_s)\ (C)(E)}$$

where A = Calibration factor for chromatographic system, in nanograms material per area unit, calculated as underivatized phenol.

B = Peak size in injection of sample extract, in area units.

V_i = Volume of eluate injected (ul)

V_t = Total volume of column eluate (ul)

V_s = Volume of water extracted (ml)

C = Volume of hexane sample solution added to cleanup column, in ml.

D = Total volume of 2-propanol extract after concentration.

E = Volume of 2-propanol extract used for derivatization.

12.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

No data available at this time.

APPENDIX C

TANNERY SUBCATEGORIES

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The tanning industry within the United States has been divided into seven subcategories by the EPA (1). A brief description of each follows.

SUBCATEGORY 1 - HAIR PULP/CHROME TAN/RETAN-WET FINISH

Tanneries within this subcategory, representing the largest portion of the leather tanning industry, process brine-cured or green-salted cattlehides into finished leather by chemically dissolving the hair (hair pulp). Three wet processing operations (beamhouse, tanyard, and retan-wet finish) produce the largest volume and heaviest pollutant loads.

Within the beamhouse operation, soaking, washing, fleshing, and unhairing are the principal contributors. This high-volume, high-strength effluent is characterized by organic matter, dissolved and suspended inorganic solids, and sulfides.

Hides are brought from the beamhouse to the tanyard for bating, pickling, and tanning. Bating delimes, reduces swelling, peptizes the fibers, removes protein degradation products, and destroys undesirable constituents in the skin (pigments and root hairs). Following the bating subprocess, hides are prepared for tanning by pickling, which provides an acidic medium to the hides for tanning agents (trivalent chromium).

The wet finishing processes (retanning, coloring, and fatliquoring) generate effluent which is generally considered high-volume and low-strength, especially as compared to the waste streams associated with beamhouse and tanyard operations.

SUBCATEGORY 2 - CATTLEHIDE/HAIR SAVE/CHROME TAN/RETAN-WET FINISH

Cattlehides in the raw or cured state are processed into finished leather by chemically loosening and mechanically removing the hair. The waste loads associated with the hair save process are characterized by high alkalinity, pH, sulfide, and nitrogen content. The remaining tanning operations (beamhouse, tanyard, and retan-wet finish) are essentially the same as Subcategory 1, and typically contribute waste loads similar in volume and strength.

SUBCATEGORY 3 - CATTLEHIDE/HAIR SAVE/NON-CHROME TAN/RETAN-WET FINISH

The process of converting cattlehides into finished leather is essentially the same as Subcategory 2. The only difference is the tanning operation itself. Cattlehides leaving the beamhouse process are bated and pickled in the same manner as in Subcategories 1 and 2. However, tanning is done primarily with vegetable tannins, alum, synthetic tanning agents, zirconium, metal salts, and other chemicals.

The significant difference in waste loads between Subcategories 1, 2, and 3, is the chromium content.

SUBCATEGORY 4 - RETAN-WET FINISH

Tanneries in this subcategory receive previously tanned hides or splits for retanning and finishing. Without the beamhouse and tanyard operations, the overall waste loads for this subcategory are substantially less than those associated with the preceding subcategories. Either chrome, vegetable, or synthetic tanning agents can be used for retanning. The waste loads associated with the wet finishing steps are similar to those for Subcategory 1.

SUBCATEGORY 5 - NO BEAMHOUSE

Tanneries receive previously unhaired and pickled cattlehides, sheepskins, or pigskins which are processed into finished leather by tanning with chrome or non-chrome agents, followed by retanning and wet finish. Since the unhairing operation is absent from these tanneries, the raw waste loads are characteristically lower than those found in Subcategories 1, 2, and 3. Because there is a tanyard operation, pollutant levels on the whole are higher than for those tanneries with retan only (Subcategory 4).

SUBCATEGORY 6 - CATTLEHIDES/THROUGH-THE-BLUE

Hair removal and chrome tanning are the basic operations used. Tanneries in this subcategory process raw and cured cattlehides to the blue tanned state only. Beamhouse operations may use either hair pulp or hair save processes. Following bating and pickling, the unhaired hides are chrome-tanned to the blue stage. The remaining operations used to produce finished leather are performed by other tanneries, such as those located in Subcategory 4.

SUBCATEGORY 7 - SHEARLINGS

This subcategory consists of tanneries which tan and wet-finish raw or cured sheepskins into finished leather with the wool intact. Because the wool is not removed, there is no beamhouse operation. The amount of foreign matter which must be removed from the wool through soaking and washing produces a high volume of wastewater characterized by higher organic waste loads than those of no-beamhouse tanneries. A degreasing subprocess is used, which is responsible for higher oil and grease loads. Tanning can be accomplished by either chrome or non-chrome. The former, however, is prevalent for shearling processing. Retanning and wet finishing follow.